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HYPERGOLIC PROPELLANTS

LIQUID AND VAPOR DISPOSAL

Phase I

Interim Report

28 December 1973

by Thomas E. Bowman and Robert W. Newman

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PREFACE

This report was prepared by Florida Institute of Technology under contract NAS 10-8399, administered by the National Aeronautics and Space Administration, John F. Kennedy Space Center, Florida. The NASA Technical Representative for the contract is Mr. Harold H. Franks, DD-MDD, and the Alternate Technical Representative is Mr. Jimmy L. Dobson, DD-MDD. This report is the first interim report, summarizing the technical effort on Phase I during the period 8 August 1973 to 19 December 1973. The contributions of Mr. James Little of F. I. T. to this report are gratefully acknowledged.

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HYPERGOLIC PROPELLANTS
LIQUID AND VAPOR DISPOSAL

By Thomas E. Bowman and Robert W. Newman

Florida Institute of Technology

SUMMARY

Our purpose in Phase I was to ascertain and catalog that which is currently being done to dispose of hypergolic propellants. To this end we contacted chemical manufacturers, users of propellants, disposal equipment manufacturers, and assorted organizations we felt might have suggestions regarding this problem.

We found that by far the most widespread means of treating all of the listed propellants for disposal is dilution followed by neutralization. Wherever possible, both fuels and oxidizers are transferred to the same holding ponds to be neutralized. Hydrazine and N_2O_4 vapors are often vented to water scrubbers, and the contaminated water is then transferred to the same holding ponds. Incinerators are used for hydrazines, and could be used for the oxidizers as well. N_2O_4 vapors are often vented through propane burners, and N_2O_4 liquid can be allowed to vaporize at atmospheric pressure. Open pit burning is still used to some extent for hydrazines, and is recommended by several authorities, subject to certain precautions.

The hydrazines present the most serious disposal problem of the substances of interest. The nitrogen-based oxidizers constitute less of a hazard, and generally methods of disposal were found to be less elaborate and rigorous in their case. Hydrogen peroxide disposal is a relatively minor problem.

In addition to destructive disposal, there were found to be possibilities for recycling some of the waste propellants, and for converting others to useful purposes. Use of the oxidizers to manufacture fertilizer seems feasible, and the hydrogen peroxide could be a valuable oxygen source in sewage treatment, and is also being considered as a replacement for chlorine in the later stages of water treatment.

I. INTRODUCTION

Many aerospace flight vehicles and spacecraft utilize hypergolic propellants. These propellants are very toxic and corrosive and require special storage, loading, and waste disposal systems. The waste disposal systems, for both hypergolic liquids and vapors, are of special concern due to problems of maintaining the quality of the environment in spite of more widespread and continuing usage of these propellants.

Existing disposal methods require re-evaluation under new program ground rules. Improvement in present methods and/or new concepts may be required in order to permit the safe disposal of these toxic liquids and vapors without contributing further to the degradation of the environment. The objective of this study, is to identify existing or develop new disposal methods, which minimize contamination of the environment, for the following hypergolic liquids and vapors:

(1) Nitrogen Tetroxide (N_2O_4)
(2) Inhibited Red Fuming Nitric Acid (IRFNA)
(3) Hydrogen Peroxide (H_2O_2)
(4) Anhydrous Hydrazine (N_2H_4)
(5) Monomethyl Hydrazine (MMH)
(6) Unsymmetrical-Dimethylhydrazine (UDMH)
(7) Aerozine 50 (50% N_2H_4 - 50% UDMH)

Phase I of the study had as its purpose identification of the current, state-of-the-art liquid and vapor disposal methods for these seven propellants. Included were a literature search, contacting typical users of the propellants, contacting manufacturers (if any) of propellant waste disposal equipment, and compilation of the accumulated information in a form suitable for evaluation in Phase II. We were concerned with the techniques currently practiced or recommended by manufacturers and users of the specified hypergolic propellants for disposing of contaminated and/or waste liquids and vapors, and also those techniques which had been discarded for one reason or another, and drawing board ideas being developed.

Phase I was not an environmental study, and was not concerned with the effect of any of these disposal methods on the environment. Rather, it was an engineering study concerned with learning the technical details of the equipment and procedures used by various organizations for hypergolic propellant disposal. In Phase II these disposal methods will be evaluated in terms of their effects on the environment, but even here the emphasis will be on identifying requirements for new technology rather than identifying any specific current environmental problems. Economic factors will also be taken into account.

II. DESCRIPTION OF PHASE I ACTIVITIES

A. The Compilation Procedure

We have compiled what we believe to be a comprehensive list of both manufacturers and users of the specified propellants from sources including Thomas Register, World Aviation Directory, Aviation Week's "Forcast and Inventory" issue of 19 May 1973, miscellaneous library sources, personal contacts, and suggestions made at the orientation meeting. We included several foreign organizations feeling that it was possible that their approaches might be substantially different from those in this country. The breakdown of activities and the foreign contacts by country are listed in Appendix A.

In the interest of completeness we compiled a list of disposal equipment manufacturers from Thomas Register and pollution control and chemical engineering journals. The fourteen chosen certainly did not constitute an exhaustive list but, rather, represented organizations we believed most likely to have been exposed to the problem of disposing of hypergolic propellants. In fact, several were subsidiaries of companies listed as users or manufacturers.

A fourth category designated simply as "Other" (see Table 1 in the following section) includes government agencies, research institutes, and one or two leads given us by respondents. As a result of additions to this list, the total contacts have increased from the original 79 mentioned in the First Monthly Status Letter to 90 at present.

The letters sent to the organizations on the original list have been included in Appendix A.

B. Response to Inquiries

Table 1 presents an overall picture of the response to our inquiry. "Positive" means a meaningful input to our study; "negative" means a response to the effect that the firm is not concerned with the listed propellants; "zero" means no response.

Only one firm actually known to be using hypergolic propellants is included in the "no response" category, and that only after repeated attempts to gain their cooperation. Others in this category are firms that have gone out of business, some that were considered remote possibilities, etc. (One thing learned in performing this study is that many "chemical companies" don't actually manufacture chemicals.) In two cases, they are organizations only recently contacted due to recent information.

Table I

Contacts & Responses by Category

Category	Response		
	Pos.	Neg.	Zero
Chemical & Manufacturers	9	9	20
Users	17	2	7
Equipment Mfg.	3	9	3
Other	6	0	4

As we had anticipated, many of the smaller chemical companies did not respond at all. Only 4 of the 18 foreign inquiries were answered, and one important foreign engine manufacturer has notified us that they are preparing a detailed report for us.

Perhaps a bit of a surprise is that the interest is so low among manufacturers of chemical disposal equipment. However, we have found that some aerospace companies are aware of the difficulties in disposing of the materials and the potential market for devices to accomplish this within present environmental controls. Indeed, travel in connection with Phase II will include trips to company sites to discuss more fully the equipment they are developing precisely for this purpose.

The Third Monthly Status Letter contained a discussion of Du Pont's interest in the use of hydrogen peroxide in sewage treatment plants. (See also the Literature Survey). Since then a representative of the Environmental Equipment Div. of FMC Corp. has discussed their interest in the possibility of using hydrogen peroxide as a replacement for chlorine in water treatment.

Two final items should be mentioned in this section. First, Rocketdyne, Div. of Rockwell International, referred us to the Waste Disposal Subcommittee, Environmental Protection Committee of the JANNAF Hazards Working Group. Contact with this subcommittee is being pursued through official NASA channels. Second, Dr. R.S. Ottinger of TRW Space Systems responded to our inquiry with two specific volumes and the summary volume of a report entitled "Recommended Methods of Reduction, Neutralization, Recovery, or Disposal of Hazardous Waste". The report is the result of a herculean effort carried out for the Environmental Protection Agency.

C. Results of the Literature Survey

The literature survey began with a computer search performed by the KSC Library, which tried all reasonable pairings of the terms "propellant", "fuel", "oxidizer", as well as the seven specific propellant names, with "disposal", "waste", and "pollution", searching back to

1966. No papers or reports were found by this method. Further work, questions to people in industry, etc., turned up one paper, two articles in in-house publications, a very significant and comprehensive study recently completed for EPA, and several technical bulletins, data sheets, etc., from the chemical industry that include recommended disposal techniques.

In addition to these reports, there are also a large number of manuals and reports from the early 1960's on the handling of these propellants. These manuals are adequately referenced by the various technical bulletins listed below, and are not included in this list; the current availability of many of them is uncertain, they are not primarily concerned with disposal, and of course they do not help in ascertaining current disposal practice. Also of interest are the sections in chemical and aerospace encyclopedias, etc., dealing with the substances of interest to this study.

The article by Chase is an early description of the incinerator built at Cape Canaveral by Thermal Research and Engineering Corp. in connection with the Titan II program. The Conner and Gebhart report describes disposal practices at the Bell Aerospace facility. Haskins' article is a very recent description of Du Pont's work with hydrogen peroxide as an oxygen source for the treatment of sewage in existing plants. The report by Ottinger et al is the result of a very large study by T R W of disposal techniques for hundreds of different hazardous materials.

In addition to these reports, a number of other papers that are of some interest for this study, but not directly related to propellant disposal, are included below as a "Secondary Bibliography". This list is of course not comprehensive, as the region of interest is essentially unbounded, but are included to simply give an entry point into some of the literature on aspects of the chemistry of these propellants that might be important to disposal considerations.

It should also be mentioned that there exists a very large and growing literature on the formation, effects, prevention, and removal of oxides of nitrogen in atmospherics discharges. This literature is of interest in connection with the disposal of either of the nitrogen-based oxidizers, although the magnitude of the releases that would be expected is certainly minute compared with current industrial and automotive problems. Oxides of nitrogen are also a potential problem with any of the incinerators, because of the use of air.

Primary Bibliography

C.E. Chase, "Automated Missile Waste Disposal". Instrumentation, Vol. 15, No. 3 (Minneapolis-Honeywell Regulator Co., Industrial Products Group, Philadelphia, Pa.)

W.J. Conner and H.W. Gebhart, "Pollutants and Pollution Control for the Agena Rocket Engine". AIAA Paper No. 71-716, presented at the 7th Propulsion Joint Specialist Conference, Salt Lake City, June 14 - 18, 1971.

James W. Haskins, Jr., "H_2O_2 Looks Good for Sewage Treatment". Innovation, Fall 1973, pp. 6-9 (E.I. Du Pont de Nemours & Co., Inc., Wilmington, Del. 19898).

R.S. Ottinger, J.L. Blumenthal, D.F. Dal Porto, G.I. Gruber, M.J. Santy, and C.C. Shih, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste". Report No. 21485-6013-RU-00, T R W Systems Group, 1 February 1973, Prepared for Environmental Protection Agency, Contract No. 68-03-0089. (See especially Vols. I, XII).

"Anhydrous Hydrazine Handling & Storage". Olin Chemicals, 745 Fifth Ave., New York, N.Y. 10022.

"Chemical Safety Data Sheet SD-5, Properties and Essential Information for Safe Handling and Use of Nitric Acid". Manufacturing Chemists' Association, 1825 Connecticut Ave., N.W., Washington, D.C. 20009, 1961.

"Chemical Safety Data Sheet SD-33, Properties and Essential Information for Safe Handling and Use of Hydrogen Peroxide". Manufacturing Chemists' Association, 1825 Connecticut Ave., N.W., Washington, D.C. 20009, 1969.

"Concentrated Hydrogen Peroxide". Bulletin No. 46, F M C Corp., Inorganic Chemicals Div., 633 Third Ave., New York, N.Y. 10017.

"Dimazine: Unsymmetrical Dimethylhydrazine". F M C Corp., Organic Chemicals Div., 633 Third Ave., New York, N.Y. 10017.

"Hercules Nitrogen Tetroxide". Product Data No. 2004, Synthetics Dept., Hercules Ave., Wilmington, Del.

"Material Safety Data Sheet: Hydrogen Peroxide 90%". F M C Corp., 1710 South Aggess Rd., Box 1056, Vancouver, Wash. 98660.

"Material Safety Data Sheet SOS-4: Nitric Acid". Synthetics Dept., Hercules Inc., Wilmington, Del. 19899.

"Material Safety Data Sheet SOS-26: Nitrogen Tetroxide". Synthetics Dept., Hercules Inc., Wilmington, Del. 19899.

"Material Safety Data Sheet: Unsymmetrical Dimethyl Hydrazine". FMC Corp., 1701 Patapsco Ave., Baltimore, Md. 21226.

"Monomethyl Hydrazine Handling and Storage". Olin Corp. Chemicals Div., 120 Long Ridge Rd., Stamford, Conn. 06904.

"Precautions and Handling Procedures for Hercules Nitrogen Tetroxide (N_2O_4)". Bulletin SI-111, Synthetics Dept., Hercules Inc., Wilmington, Del. 19899.

Secondary Bibliography

Anon., "Nitric Acid Producers Ponder New Technology". Chemical Engineering, Dec. 15, 1969, p. 50.

Anon., "Nitric Acid Rolls On". Chemical Engineering, June 29, 1970, pp. 24 - 25.

D.S. Burgess, G.H. Martindill, J.N. Murphy, F.J. Perzak, J.M. Singer, and R.W. Van Dolah, "Inerting and Extinguishment of Aerozine-50 with Water and/or CF_3Br." J. Spacecraft, Vol. 6, 1969, pp. 1259-1268.

Theodore Christos, Yael Miron, Harry James and Henry Perlee, "Combustion Characteristics of Condensed-Phase Hydrazine-Type Fuels with Nitrogen Tetroxide". J. Spacecraft, Vol. 4, 1967, pp. 1224-1229.

H. Greer, "Vacuum Starting of Reactors for Catalytics Decomposition of Hydrazine". J. Spacecraft, Vol. 7, 1970, pp. 522-528.

H. Greer, S.M. King, P.C. Marks, and D. Taylor, "Experimental Evaluation of Catalysts for Monopropellant Hydrazine Propulsion." J. Spacecraft, Vol 8, 1971, pp. 105-110.

M.H. Heinz and G.F. Orton, "Effects of Sterilization and Decontamination on Hydrazine Propulsion Systems." J. Spacecraft, Vol. 6, 1969, pp. 853-855.

Frend J. Miner and Paul G. Hagan, "Rate of Hydrogen Peroxide Decomposition in Nitric Acid Solutions." Ind. Eng. Chem. Process Des. Develop., Vol. 11, 1972, pp. 547-549.

D.J. Newman, "Nitric Acid Plant Pollutants." Chemical Engineering Progress, Vol. 67, 1971, pp. 79-84.

Michel A. Saad and Michael B. Detweiler, "Analysis of N_2H_4 - RFNA Reaction Product." AIAA Journal, Vol. 7, 1969, pp. 1588-1592.

Michel A. Saad, Michael B. Detweiler, and Michael A. Sweeney, "Analysis of Reaction Products of Nitrogen Tetroxide with Hydrazines under Non-ignition Conditions". AIAA Journal, Vol. 10, 1972, pp. 1073-1078.

Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition. Interscience Publishers, New York 1966.

III. The Accumulated Data

Detailed results of the study are recorded in Appendix B, "Final Work Sheets." Included there are both current practices and recommendations from various sources. The purpose of this section is to present these results in a more succinct fashion, rather than separating the information according to source. In this section, the propellants will be treated in four groups, rather then seven: hydrazines, hydrogen peroxide, nitrogen tetroxide, and red fuming nitric acid. The reason for combining the hydrazines is that the differences in disposal methods between the various hydrazines were so minor that there is really no reason to discuss them separately.

A. Hydrazines

1. Incineration

Two organizations are currently incinerating aqueous solutions of hydrazines (and, in one particular instance, a solution of MMH in isopropyl alcohol). One incinerator uses natural gas as primary fuel and maintains a flame temperature of 1900 F; the other uses diesel fuel and maintains 2700 F or higher (3200 F was also mentioned.) The TRW study recommended controlled incineration with effluent scrubbing to eliminate any ammonia formed in the combustion process.

2. Neutralization

A number of organizations dispose of hydrazines by dilution followed by neutralization. The chemical industry recommends neutralization using calcium hypochlorite or a dilute solution of hydrogen peroxide, catalyzed by a trace amount of copper sulfate. Dilute hydrochloric or sulfuric acid is also recommended in the case of MMH, and atmospheric oxygen in the presence of copper salts for N_2H_4.

The catalyzed hydrogen peroxide reaction is currently being used by several of the organizations contacted, but not, as far as we could ascertain, the calcium hypochlorite or hydrochloric or sulfuric acid reactions. Two organizations precede the hydrogen peroxide reaction with a sodium hydroxide reaction, and at least one uses sodium hydroxide alone to treat dilute hydrazine wastes. Also used for neutralization purposes are dilute nitrogen tetroxide, sodium hypochlorite , and hydroxyacetic acid. (Nitrogen tetroxide is often used in a de facto manner simply because the same holding ponds are used for both fuel and oxidizer wastes.)

Hydrazine vapors are often sent through water-spray scrubbers, and the water then treated by one of these neutralization reactions.

Atmospheric air (bubbling through the dilute solution) was mentioned by several people as a sensible solution, but seems to be used by only one organization at the present time. Ozone was also mentioned as an alternative to air.

3. Open Pit Burning

Open pit burning is recommended by the chemical industry for disposal of large quantities of hydrazines, and is in fairly widespread use still, although it seems to be much less prevalent now than several years ago. The TRW study labeled this method "generally acceptable" but warned of excessive NO_x generation. Concentrations less than 40% are not combustible, and other contaminants might also pose a problem.

4. Catalytic Decomposition

As far as we could ascertain, this method is not being used anywhere, and would seem impractical in terms of both cost and the problems of catalyst poisoning. The TRW study, however, mentions the possibility of a new low-cost catalyst that might merit further study.

5. Other Methods

Direct reaction with N_2O_4 has been used by at least two organizations. Mixing small quantities of slightly out-of-specification hydrazine in with large amounts of non-contaminated hydrazine is an obvious solution where the volumes are large amough to make this feasible. Filtration to remove suspended particulate matter can also return hydrazine to specification. Return to a chemical company is a possibility. Venting of vapors to the atmosphere is common, often with more or less elaborate precautions, including consideration of mixing models, etc. One organization uses vapor re-condensers on tall vent stacks to recover some of the vapors. Dilution followed by pouring on the ground is still used, but not to any great extent.

B. Hydrogen Peroxide

Neither the chemical industry nor the TRW study recommends anything more elaborate than dilution with water and pouring on the ground or into a drainage system, and these procedures are commonly followed. One organization speeds the decomposition using a catalyst - either platinum or silver screen in the case of small quantities, or Na OH for larger quantities.

Actually, disposal of significant quantities of H_2O_2 might not normally be necessary in view of its possible application in virtually any sewage treatment plant.

C. Nitrogen Tetroxide

1. Incineration

Although not currently being practiced, as far as we could learn, incineration has been accomplished successfully in the past and appears feasible. It is not practiced, in all probability, because of the relative ease of other means of disposal. N_2O_4 does have a low boiling point - standard atmospheric temperature and pressure, approximately - and the vapors are vented through propane burners by several of the organizations contacted, apparently with very good success.

2. Neutralization

By far the most common means of disposing is dilution followed by neutralization. The chemical industry recommends soda ash, lime, or other alkali for neutralization. Substances used by the organizations contacted include sodium carbonate, triethanolamine, and sodium hydroxide. Several have diluted and added the misture to the same holding ponds used for hydrazines; these ponds were then neutralized using sodium hydroxide or hydrogen peroxide with the copper sulfate catalyst, or both.

Vapors are sometimes treated in water-spray or baking soda scrubbers, or bubbled through water. The watter effluent is sent to holding ponds to be neutralized as above.

3. Other Methods

One organization consumes waste N_2O_4 in combustion with hydrocarbons or other fuels. Some waste N_2O_4 has been returned to the manufacturer. Vapors are often vented to atmosphere, sometimes with more or less elaborate precautions as with the hydrazines.

D. Inhibited Red Fuming Nitric Acid

Treatment is invariably the same as for N_2O_4, except that in the case of IRFNA taking part in a combustion reaction, the product gases should be treated by water scrubbing to avoid HF emissions. The TRW study agrees, but also mentions the possibilities of reaction with ammonium hydroxide to form an ammonium nitrate solution which can be used as a fertilizer, and steam distillation to yield concentrated acid.

APPENDIX A

THE ORGANIZATIONS CONTACTED

A - I INITIAL CONTACT LIST

The initial list contained 65 possible users of hypergolic propellants; due to secondary references, etc., the list has grown to 90. Every effort was made to make the list as comprehensive as possible, with the understanding that we would elicit negative responses from many of the organizations - especially some of the smaller chemical companies. We also attempted to include as many foreign organizations as possible, feeling that it was quite possible that their approaches to disposal might differ substantially from those used in this country.

On the basis of what we knew of their activities, the initial list was divided as follows (with some organizations involved with more than one propellant):

Hydrazines (all varieties):	43
MMH:	8
UDMH:	8
Aerozine 50:	9
Hydrogen Peroxide:	16
Nitrogen Tetroxide:	15
RFNA:	7
Catalysts:	3

Of the 65 organizations listed, 35 were chemical companies, and the remainder were primarily users of hypergolic propellants. The foreign companies and organizations listed were based in the following countries:

France:	5
Germany:	4
Britain:	2
Japan:	4
Sweden:	2
Spain:	1

The cooperation of all the organizations that provided us with useful information (see list in following section) is most gratefully acknowledged.

A - II LIST OF COOPERATING ORGANIZATIONS

Aerojet Liquid Rocket Co., Sacramento, California
Allied Chemical Corp., New York, N.Y.
Battelle Columbus Laboratories, Columbus, Ohio
Battelle Pacific Northwest Laboratory, Richland, Washington
Bell Aerospace Co., Buffalo, New York
The Boeing Company, Seattle, Washington
E.I. Du Pont de Nemours and Co., Inc., Wilmington, Delaware
Fairmount Chemical Co., Newark, N.J.
Fisons Ltd., Cambridge, England
FMC Corp., New York, New York
Hercules, Inc., Wilmington, Delaware
Instel Corp., New York, New York
Lockheed Missiles and Space Co., Sunnyvale, California
Marquardt Co., Van Nuys, California
Martin-Marietta Corp., Denver, Colorado, and Vandenberg AFB, Calif.
NASA - Johnson Space Center, Houston, Texas
NASA - Western Test Range
NASA - White Sands, New Mexico
Olin Chemicals, Stamford, Conn.
Pan American World Airways, Cape Canaveral, Florida
PPG Industries Inc., Pittsburgh, Pa.
Rockwell International, Rocketdyne Div., Canoga Park, California
Rockwell International, Space Div., Downey, California
SAAB - Scania Ab, Linkoping, Sweden
Shell Development Co., Houston, Texas
Sundstrand Aviation, Rockford, Illinois
Thermal Research and Engineering Corp., Wilmington, Delaware
Tri-Mer Corp., Owosso, Michigan
TRW Systems, Redondo Beach, California
United Aircraft, Hamilton Standard Div., Windsor Locks, Conn.
United Aircraft, United Technology Center, Sunnyvale, California
Volvo Flygmotor Ab, Trollhattan, Sweden
Walter Kidde and Co., Inc., Belleville, New Jersey

We would also like to thank the many other companies who wrote or telephoned to let us know that they had no significant information to contribute.

A - III INITIAL LETTERS OF INQUIRY

On the following pages are copies of the letters initially sent out to the companies on the contact list. Separate letters were sent to pollution control equipment manufacturers and overseas firms, as shown.

FLORIDA INSTITUTE OF TECHNOLOGY

MELBOURNE, FLORIDA 32901

Department of Mechanical Engineering

Phone: (305) 723-3701

August 15, 1973

Florida Institute of Technology has been contracted by National Aeronautics and Space Administration, J. F. Kennedy Space Center (NAS 10-8399) to evaluate existing disposal methods for hypergolic propellants (both liquid and vapor phases) with the aim of determining the best method/methods of disposal, and defining new concepts where desirable. The program calls for a determination of the state of the art, followed by an evaluation of all current practices to determine which are the most ecologically and economically effective methods, for disposing of the following propellants:

1. Nitrogen tetroxide
2. IRFNA
3. Hydrogen Peroxide
4. Anhydrous Hydrazine
5. MMH
6. Aerozine 50
7. UDMH

In this regard we are contacting manufacturers and users of hypergols and manufacturers of pollution detection and control equipment to compile information on disposal techniques that are in use, or rejected for one reason or another.

We recognize that because of current emphasis on environmental problems this is a very sensitive area and that those dealing with potential pollutants might understandably be hesitant to discuss disposal practice. Therefore, we can assure you that any information you designate as proprietary will be treated accordingly, and that all means of reporting data will use code designation rather than identifying the specific organization involved. Also, we would emphasize that this is an engineering study looking for solutions to a problem and is not an environmental study.

Specifically we are in need of detailed information on techniques you have used and discarded, those you've discarded before use, those you are currently using, and those you plan to use to dispose of other than small laboratory samples of the cited propellants. Any in-house reports or papers published in the open literature that deal with the handling of these hypergols would be most helpful and certainly appreciated. To assist us in making this study as comprehensive as possible, we would also appreciate your suggestions of names of people in other organizations who might be familiar with disposal techniques for these propellants.

Please advise whether or not you believe that a visit to your plant to discuss the various aspects of this problem would be fruitful. We believe that the results of this effort will be useful to both manufacturers and users of hypergolic propellants and, therefore, we plan to keep contributing organizations informed of meaningful progress. Please let us know if you wish to be included on the mailing list.

Thanks very much for your cooperation.

Sincerely,

R.W. Newman, Assistant Professor

T.E. Bowman, Associate Professor
Program Manager

RN:jk

FLORIDA INSTITUTE OF TECHNOLOGY

MELBOURNE, FLORIDA 32901

Department of Mechanical Engineering

Phone: (305) 723-3701

August 15, 1973

Florida Institute of Technology has been contracted by National Aeronautics and Space Administration, J. F. Kennedy Space Center (NAS 10-8399) to evaluate existing disposal methods for hypergolic propellants (both liquid and vapor phases) with the aim of determining the best method/methods of disposal, and defining new concepts where desirable. The program calls for a determination of the state of the art, followed by an evaluation of all current practices to determine which are the most ecologically and economically effective methods for disposing of the following propellants:

1. Nitrogen tetroxide
2. IRFNA
3. Hydrogen Peroxide
4. Anhydrous Hydrazine
5. MMH
6. Aerozine 50
7. UDMH

In this regard we are contacting manufacturers and users of hypergols and manufacturers of pollution detection and control equipment to compile information on disposal techniques that are in use, or rejected for one reason or another.

Specifically we are in need of detailed information on techniques, apparatus, and instrumentation that you have designed and used for measuring, treating, and disposing of the cited propellants. Any in-house reports or papers published in the open literature would be most helpful and certainly appreciated.

Since we are limiting ourselves to such a narrow and perhaps uncommon problem, it is extremely difficult to discern just which organizations would be involved and knowledgeable. We are attempting to make this study as comprehensive as possible; to this end we would greatly appreciate your assistance in suggesting names of other organizations that might be able to contribute information.

We believe the results of this effort will be useful to the pollution control industry as well as to the manufacturers and users of these hypergolic propellants. Hence, we plan to keep contributing organizations informed of meaningful progress. Please let us know if you wish to be included on the mailing list.

Thanks very much for your cooperation.

Sincerely,

R. W. Newman

R. W. Newman, Assistant Professor

T. E. Bowman

T. E. Bowman, Associate Professor
Program Manager

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Phone: (305) 723-3701

August 22, 1973

Florida Institute of Technology is currently performing a study, under Contract NAS 10-8399 with the National Aeronautics and Space Administration's John F. Kennedy Space Center, to evaluate methods of disposing of seven hypergolic rocket propellants. Objective of the study is to determine the best methods of disposal for each of the following propellants, in both liquid and vapor form:

1. Nitrogen Tetroxide, N_2O_4
2. Red Fuming Nitric Acid, $HNO_3 + NO_2 + H_2O$
3. Hydrogen Peroxide, H_2O_2
4. Anhydrous Hydrazine, N_2H_4
5. Monomethyl Hydrazine (MMH), CH_3NHNH_2
6. Unsymmetrical - Dimethylhydrazine (UDMH), $(CH_3)_2NNH_2$
7. Aerozine 50 (50% N_2H_4 + 50% UDMH)

The study involves a detailed determination of the current state of the art, followed by evaluation of all current practices to determine which are the most ecologically and economically effective, and culminating in definition of new disposal techniques where desirable. In this regard we are contacting manufacturers and users of these propellants to compile information on disposal techniques that are currently in use, or that have been used in the past, or are being considered for future use. We are particularly interested in learning of any disposal techniques used in Europe or Japan that might differ from prevailing American practice, and in learning of any studies or reports dealing with propellant disposal techniques. To assist us in making this study as comprehensive as possible, we would also appreciate your suggestions of names of people in other organizations who might be familiar with disposal techniques for these propellants.

We recognize that this is a very sensitive area and that those dealing with potential pollutants might understandably be hesitant to discuss disposal practice. Therefore, we can assure you that any information you designate as proprietary will be treated accordingly, and that all means of reporting data will use code designation rather than identifying the specific organization involved. Also, we would emphasize that this is an engineering study looking for solutions to a problem and is not an environmental study.

We believe that the results of this effort will be useful to both manufacturers and users of hypergolic propellants, and therefore, we plan to keep contributing organizations informed of meaningful progress. Please let us know if you wish to be included on the mailing list.

Thanks very much for your cooperation.

Yours Sincerely,

Thomas E. Bowman
Associate Professor
Study Manager

TEB:jk

APPENDIX B

Final Work Sheets

B-I: DISPOSAL METHODS RECOMMENDED BY THE CHEMICAL INDUSTRY

These methods are taken from the technical bulletins and data sheets listed in the Literature Survey, Section II-C of the report.

1. Anhydrous Hydrazine (Source of information: Olin Chemicals)

"Waste hydrazine from spills or process effluent presents a problem of neutralization prior to sewering. Commercial calcium hypochlorite, containing 70% available chlorine, (HTH) provides an ideal solution to this problem. The reaction between the hydrazine and calcium hypochlorite yields nitrogen and calcium chloride. Other decontaminants may also be used (see Table III).

"Drains from areas of hydrazine handling should lead to a sump or holding pond where neutralization can be effected in a very dilute solution. One mole of calcium hypochlorite is required per mole of hydrazine. On a weight basis this is equivalent to 6.4 pounds of HTH per pound of hydrazine. Recommended usage is seven to ten pounds of HTH per pound of hydrazine to provide an excess of HTH. This is roughly equivalent to 0.6 to 1.0 per pound of HTH per gallon of 1% solution of hydrazine.

"Neutralization of hydrazine with HTH is complete and rapid at pH 5.0 to 8.0. At lower pH, the reaction is complete, but may require a longer period of time. At higher pH, the reaction may not proceed to completion.

"A dilute solution of hydrogen peroxide may also be used to neutralize dilute hydrazine wastes. One mole of hydrogen peroxide is required per mole of hydrazine. A slight excess of peroxide is recommended to ensure complete destruction of the hydrazine. The addition of a trace amount of copper sulfate will catalyze the reaction, causing it to proceed more rapidly.

" For larger quantities, disposal is usually carried out by burning in increments in a small, concrete-lined pit. Hydrazine and aqueous solutions of hydrazine are placed in the pit by means of a pipe or surface channel. The hydrazine can be ignited by an igniter (squib-fired), an oxidizer such as nitrogen tetroxide, or a torch. Concentrations as low as 40 percent by weight hydrazine in water can be burned. Concentrations lower than 40% can be burned by enriching the dilute mixture with a soluble flammable liquid, such as alcohol."

Table III. Decontaminants for Hydrazine Investigation *

Decontaminant	Possible Reaction Products	Approx. Heat Liberated Kcal/Mole N_2H_4
H_2O	$N_2H_4 \cdot xH_2O$	3.9
$NaHCO_3$	$(N_2H_5)_2CO_3$ Na_2CO_3	10
H_3BO_3	A salt	5
$KMnO_4$	N_2	177
H_2O_2	NH_3, N_3H	91-121
Cl_2 gas/HTH	N_2	160/177

* F. E. Scott, J. J. Burns, and B. Lewis, "Explosive Properties of Hydrazine." Report on Investigations 4460, U.S. Dept. of the Interior, Bureau of Mines, Pittsburgh, Pa., May 1949.

2. Monomethyl Hydrazine (Source of information: Olin Chemicals)
"To reduce fire hazards, spilled MMH may be diluted with large amounts of water and neutralized by dilute hydro-chloride acid or sulfuric acid. This procedure ensures the trapping of MMH vapors and forms a MMH-type salt.

"Diluted MMH, while no longer a fire hazard, may still be dangerour if not disposed of properly. MMH must not be permitted to drain into a potable water system. Provisions must be made to permit liquid drainage into a disposal area where it may be burned in small increments or decomposed by a chemical decontaminant such as calcium hypochlorite (HTH ™) or hydrogen peroxide.

"Empty drums and containers should be rinsed with water and steamed for 15 minutes to remove toxic and flammable vapor."

3. UDMH (here referred to by the trade name "Dimazine")
(Source of information: FMC Corp.)

"Equipment can generally be decontaminated rather simply by thorough flushing with large volumes of water or with dilute acid. It may be conveniently steamed thereafter. It should, of course, be thoroughly dried prior to return to Dimazine * service, making sure that no water has been trapped at low points in the system.

"Our suggestion for deliberate destruction of comparatively large quantities of Dimazine is to burn it under proper supervision and safeguard. This technique has been successfully used in the field. Small quantities such as minor spills, etc., usually can be disposed of most conveniently through sewering with water.

"Copious water flushing is recommended for personnel decontamination. Other comment on personal hygiene appears within the immediately following section."

4. Hydrogen Peroxide (Source of information: Manufacturing Chemists Association)

"Hydrogen peroxide is an exceptionally pure product and contains no contaminants that would cause surface water pollution, or interference with sewage. Its decomposition products are pure water and oxygen. However, strong hydrogen peroxide should be diluted with copious quantities of water before disposal to prevent strong reaction with organic materials and to prevent injury to fish life since there is some evidence that high concentrations of hydrogen peroxide are harmful to certain fish. (See "Treatment of Water Waters Containing Hydrogen Peroxide, Hydrazine, and Methanol." Chemistry and Industry, 1951, 1104-6.) Since certain agencies of local, State, and Federal governments have been established to protect our streams, all rules and regulations applying to a given location should be ascertained and observed.

"The treatment of a decomposing container of hydrogen peroxide will depend upon several factors, such as the stage at which the decomposition is first discovered, the degree of contamination as indicated by the rate of temperature rise and the volume of hydrogen peroxide concerned. It should be noted that the rate of decomposition increases exponentially with temperature, 1.5 times for each 10° F. rise. Any container of hydrogen peroxide, if grossly contaminated, might rupture from decomposition pressure, or be subject to vapor explosion above the peroxide, if excessive temperatures are reached. . .

"A drum of unstable hydrogen peroxide should be taken quickly to an isolated place, uncapped, and either overflowed with a water hose or tipped over and emptied as fast as possible, washing the peroxide away with plenty of water. However, if it has reached the point of boiling, or spewing steam from the vent, personnel should evacuate to a safe distance since the drum will probably rupture violently within a few minutes. When this occurs the area should be washed down liberally with water.

"A decomposing tank of hydrogen peroxide requires different treatment. Decomposition is evidenced by self-heating or bubble action. The addition of phosphoric acid (reagent grade - 1 lb. for each 100 gals. of H_2O_2 solution) may arrest the decomposition at this early stage. The tank should be watched very closely and precautions taken in case decomposition is not checked.

"If the temperature of the tank continues to rise its contents should be disposed of before it reaches a point 15° F higher than the surroundings. A clean fire hose, without brass or iron fittings, should be inserted through the tank manhole to the bottom of the tank and the tank's concents diluted with a large amount of water and discharged as fast as possible by overflowing through the manhole or other means. This whole operation is facilitated if the tank is equipped with an aluminum deluge pipe reaching to the bottom of the tank with a remote coupling for water. In any event, loss of the peroxide is preferable to loss of the tank itself.

"Discarded peroxide from either a drum or tank should go to an open body of water or drainage ditch, preferably containing water. If any peroxide goes into a sewer or closed drain, there should be no combustibles present and large volumes of water should be added to the drain along with the peroxide."

5. Nitrogen Tetroxide (Source: Hercules Inc.)

"Spills should be flushed to a collection sump and neutralized with soda ash or other alkali."

Also, "Transfer to salvage vessel. Neutralize with soda ash or lime. Keep from sewer or streams."

6. Nitric Acid

(First source: Manufacturing Chemists Association)
"Dilute and neutralize before disposal. Do not flush down drains where the acid will eventually pollute streams, city sewage systems, etc."

(Second source: Hercules Inc.)
"Neutralize with soda ash or lime."

B - II. DISPOSAL RECOMMENDATIONS FROM THE TRW STUDY

All material in this section is taken directly from TRW Report No. 21485-6013-RU-00, prepared for the Environmental Protection Agency, by R.S. Ottinger et al (see the Literature Survey, Section II-C of this report.)

1. Hydrazine

Hydrazine as a waste will generally be encountered as excess material, as contaminated material from spills, or in aqueous streams from chemical process industries. Because of the hazards involved (unpredictable decomposition), hydrazine is usually not recovered in a concentrated form from contaminated or dilute systems. In ponds or holding tanks dilute hydrazine is decomposed by the air and bacteria into nitrogen, hydrogen, water and ammonia. In a concentrated form, hydrazine is destroyed by burning.

The safe disposal of hydrazine is defined in terms of the recommended provisional limits in the atmosphere, water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Hydrazine	0.01 ppm	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Hydrazine	1.0 ppm	Quantity will rapidly oxidize to near-zero concentration

Hydrazine is generally destroyed by oxidation to water and nitrogen. In dilute solution, dissolved oxygen, catalysis, or bacterial action convert hydrazine to nitrogen, hydrogen, ammonia and water. Therefore, there are no problems in dealing with the products from waste treatment. Current disposal practices for hydrazine are briefly described in the following paragraphs together with recommendations as to adequacy.

Option No. 1 - Open Pit Burning

Hydrazine poured into an open lined pit is burned to nitrogen and water. The transfer of the hydrazine and the ignition must be accomplished by a remote means. For drum quantities of hydrazine this method is generally acceptable although since excessive NO_x might be generated another option would be preferred.

Option No. 2 - Incineration

The Air Force has a minimum of ten trailer-mounted incinerators capable of incinerating up to 6 GPM of hydrazine in a variety of mixtures with water (from 100 percent hydrazine to 100 percent water). The effluents from the units is limited to 0.03 lbs/min NO_x when incinerating hydrazine. These units are acceptable for disposing of large quantities of hydrazine.

Option No. 3 - Catalytic Decomposition

One of the applications for hydrazine is its use as a monopropellant. When hydrazine is passed over a support (usually aluminum oxide) coated with certain metals or metal oxides, it is decomposed into nitrogen, hydrogen and ammonia. The details of catalyst composition are usually found in the classified literature. In most cases the catalyst is expensive, but TRW Systems has preliminary data on a low cost catalyst that should be further investigated.

Recommended Treatment: Controlled incineration with facilities for effluent scrubbing to abate any ammonia formed in the combustion process.

2. Hydrogen Peroxide

Concentrated hydrogen peroxide is a powerful oxidizing agent. Rapid decomposition is hazardous. Wasted concentrated hydrogen peroxide can be disposed of by dilution with water to release the oxygen. Agitation would accelerate the decomposition. After decomposition, the waste stream may be discharged safely.

3. Nitric Acid

Waste streams containing acids, acidic oxides, or bases can be treated by neutralization (1) to form a neutral solution which can then be discharged safely, or (2) to yield an insoluble precipitate which can be removed by filtration.

For the acids, acidic oxides and halides, soda ash-slaked lime solution is most commonly used. In the case of nitric and hydrochloric acids, the neutral solution of nitrate or chloride of sodium and calcium is formed and can be discharged after dilution with water.

Ammonium hydroxide may be neutralized by nitric acid to form a solution of ammonium nitrate which can be used as fertilizer.

Nitric acid forms a constant-boiling azeotrope with water (68 % HNO_3 + 32% H_2O). The normal boiling point of the azeotrope is 120.5°C. Hence, under certain conditions, spent nitric acid can be recovered by steam distillation to yield concentrated acid.

Recommended treatment: Soda ash-slaked lime is added to form the neutral solutioon of nitrate of sodium and calcium. This solution can be discharged after dilution with water.

B-III: CURRENT DISPOSAL PRACTICES

This section lists, propellant by propellant and company by company for each propellant, the actual current disposal practices for each organization, insofar as we have been able to ascertain them. In order to facilitate our access to frank, correct, and detailed information, all cooperating organizations were promised that the information furnished would not be identified as to source. For that reason, all organizations are referred to below in terms of a number, chosen more or less at random, rather than by the organization name. Disposal practices at the Western Test Range, because of the rather complex nature of the inter-relationship of the various organizations operating there, are treated separately at the end of this section.

It should be mentioned that the level of activity in hypergolic propellant disposal is clearly much lower now than several years ago; some organizations that formerly handled large quantities of these propellants as part of their everyday routine have not handled significant quantities for some time, and many of the people who were most familiar with propellant disposal practices are now gone. On the other hand, those organizations still involved with hypergolic propellants have by and large improved and refined their disposal practices considerably over the past several years.

In the list that follows, the treatment of hydrazines posed a problem. We are specifically interested in four types of hydrazine propellants: N_2H_4, MMH, UDMH, and Aerozine 50 (50%, N_2H_4, 50%, UDMH.) Most disposal practices, however, do not differentiate between the various hydrazines - an incinerator or holding pond used for hydrazines, for example, will normally be used for any of the hydrazines needing disposal, without discrimination. For that reason, the following list first treats disposal methods that seem to be used for any hydrazine the organization needs to dispose of. The following sections pertaining to specific hydrazines include only additional information not included in the first section. There is no separate section for Aerozine 50 or UDMH, since we have discovered no disposal techniques that are specifically applicable to these propellants and not to other hydrazines.

Primary attention on the part of most of the cooperating organizations was given to liquid disposal, as indicated below, with vapors often given little attention.

N_2O_4 is the only propellant of interest that will boil away if left unpressurized in a warm environment (its boiling point is 70.1° F (21.15°C) at 1 atm), although RFNA gives off NO_2 vapors (the "fumes"). UDMH has the lowest boiling point of the three hydrazines: 146° F (63°C) at 1 atm.

Past practices (since discontinued) mentioned by several organizations, such as pouring waste propellants on the ground in remote areas, etc., are not included in the following list. In addition, simple venting of vapors to the atmosphere and transferring deluge water to holding ponds until evaporated, without other treatment, were mentioned by several organizations in connection with all the propellants, and are also not included in the list. The more significant current practices that were reported to us are listed below.

1. Hydrazines - General

   a. Liquid

      #9 burns small quantities in air or with N_2O_4

      #11 dilutes concentrated wastes with water (at least to 50%) and burns with excess air in a combustion chamber designed for the purpose. The combustion consists essentially of a fire-brick heat sink which is preheated with propane to provide positive ignition and insure complete combustion. Water based flush fluids and similar low concentration wastes are dumped into one of two holding ponds. One is a square pit agitated by bubbling compressed air at two points; the other is a ditch extending about one mile past the point at which it last receives effluent. Because of addition of oxidizer wastes to the same holding ponds, the contents are normally acidic; automatic monitoring and neutralizing stations at each pond measure the pH and add NaOH solution until the pH exceeds 6.5. At this point, the station automatically begins pumping fluid from the pond over the dam until the pH again drops.

      #27 burns waste hydrazines in an incinerator, by over-stoichiometric burning followed by a water quench to 2000° F and reburning to eliminate CO and H_2 products.

#29 amounts of less than one gallon are diluted with water and neutralized. Quantities larger than one gallon are disposed of through "licensed disposal companies." Some wastes are consumed by burning if the propellant plus contaminant will support combustion.

#33 uses large enough quantities that it is feasible to mix out of specification hydrazines back in with the main supply without seriously degrading the main supply. They have also disposed through combustion in a simulated rocket engine with N_2O_4.

#34 open pit burning in a remote area; combustion is initiated by throwing in a burning towel. In addition, spills are flushed with volumes of water to a concrete-lined lagoon, where hydrogen peroxide and copper sulfate catalyst are added.

#36 uses a water deluge system and a large fume scrubber to capture all hypergols. They are neutralized in underground sumps and then consigned to a disposal contractor equipped with tank trucks for final disposition.

#37 small quantities are disposed of by burning; larger quantities are turned over to another organization on this list for disposal in an incinerator.

#49 disposes of aqueous solutions with hydrazine concentrations between 1% and 40% in an incinerator, fired by diesel fuel, at 2700°F. Contaminated fuels, (which may contain small amounts of oxidizer or flush fluids) are collected in a holding pond, diluted to 40% fuel or less if necessary, and fed to the incinerator. Wastes with less than a 1% concentration of fuel are chemically treated as follows:

(1) .01 pound of copper sulfate is added for each 1000 gallons of waste.

(2) The pH is adjusted to between 7.0 and 8.5 by adding a 50% solution of NaOH, or nitric or sulfuric acid, as required.

(3) Hydrogen peroxide (35% strength) is added.

(4) After mixing, the fuel concentration should be less than 0.5 ppm, and the pH between 6.0 and 8.0. If so, the wastes are surface drained; if not, the procedure is repeated starting at step (2).

#76 flushes with water and drains to an open sump; contaminated propellant may also be added directly to the sump. Contents of the sump are periodically disposed of in an incinerator, fired by natural gas, at 1900°F.

#89 dilutes with water and transfers to a holding pond, where it is neutralized with N_2O_4.

#90 uses a small holding pond, where it is neutralized with H_2O_2.

b. Vapors

#11 vents to atmosphere but does not risk releasing unless atmospheric conditions will reduce contaminant concentrations below threshold limit values. This determination is based on data taken at micrometeorological stations at each vent site on wind direction, velocity, gustiness, and thermal lapse rate at 2 ft., 50 ft. and 100 ft. from ground level. Prediction is based on standard mixing models, modified by empirical corrections for local conditions.

#33 pressurizes vapors with N_2 and vents through a scrubber. Water from the scrubber is flushed down trenches to a 100,000 gallon concrete holding pond, which is agitated by a recirculating pump. pH in the holding pond is normally on the acid side; NaOH is added to neutralize it and a reagent used to check for free hydrazine radicals. If too many are present, copper sulfate and dilute H_2O_2 are added. When the contents look good, they are pumped out to a series of holding ponds stairstepping down the side of a hill, all of which are continually monitored. Deep water wells in the area are also periodically checked. (This system relies on abundant supplies of water and good laboratory backup). The scrubber is a 14 inch diameter stainless steel pipe, 20 feet long, with water spray. Originally, a stainless steel tub with

a tall stack was tried, as well as a recirculating NaOH spray rather than water spray. Another variation is an aspirator, in which vent vapors are entrained in the water flow at a number of low pressure points.

#34 vents to atmosphere through tall vent stacks equipped with vapor re-condensers that return some liquid to the supply.

2. Anhydrous Hydrazine (N_2H_4)

a. Liquid

#30 dilutes 100 to 1 with water and drains into the ground. A neutralization system consisting of a series of trenches and two 1500 gallon holding tanks is being constructed. The material in the holding tanks will be neutralized with a 12 1/2% solution of sodium hypochlorite. When free Cl^- is sensed in the solution the neutralized material will be drained from the tanks to a pond.

#31 burns off small quantities in a 10 ft. by 20 ft. steel pan, ignited by a gas flame.

3. Monomethyl Hydrazine (MMH)

a. Liquid

#36 neutralizes small amounts using hydroxyacetic acid.

#37 flushes residuals with isopropyl alcohol and transfers to another organization on this list for disposal in an incinerator.

4. Hydrogen Peroxide (H_2O_2)

a. Liquid

#9 pours on bare ground and flushes with water.

#31 dilutes at least 100 to 1 with water and then flushes into the sewer system.

#33, #34, #49, and #90 use H_2O_2 to aid in disposal of hydrazines, and for treating holding ponds.

#78 disposes of small quantities in the laboratory using a platinum or silver screen as catalyst. Large quantities are diluted with water to between 25% and 40% H_2O_2 and decomposed by catalyzing with caustic. At 212° F and a caustic level of 0.5 - 1% NaOH, decomposition is more than 95% complete in one hour.

#82 has diluted small quantities with water and discarded to the drainage system.

5. Nitrogen Tetroxide (N_2O_4)

a. Liquid

#9 dilutes with water and neutralizes with sodium carbonate, or alternatively burns with hydrocarbons or other fuels.

#11 pre-dilutes with water and dumps into the same holding ponds that receive dilute hydrazines; see Hydrazines - General for additional description and treatment.

#29 treatment as described under Hydrazines - General.

#33 dilutes and adds to holding pond - see Hydrazines - General for additional description and treatment. Alternatively, allows to vaporize; see following section for treatment of vapors.

#34 pours small quantities into the concrete-lined lagoon mentioned above under Hydrazines - General. Alternatively, it is allowed to vaporize and treated as described in the following section.

#36 has neutralized small quantities with triethanolamine. Larger quantities (roughly 8 gallons) caused violent reaction with triethanolamine and explosion. Currently both neat N_2O_4 and halocarbon solvent contaminated with N_2O_4 are shipped to the NASA facility at White Sands, N.M. for disposal. This organization also attempted to use Molecular Sieve 13X material, on the recommendation of another organization; their experience was that the material is permanently degraded by N_2O_4 contact and that violent reaction is likely.

#37 transfers their waste to other organizations on this list for disposal. In addition, small quantities are wiped up with a neutralized (sodium bicarbonate) wet sponge. The sponges are then placed in a neutralized solution contained in a stainless steel bucket. This solution is subsequently disposed of by a commercial disposal service. Residuals are flushed with Freon MF and dumped into a holding tank for later disposal by a commercial disposal service company.

#38 has returned N_2O_4 to Hercules Inc.

#49 dilutes to less than 5% concentration and neutralizes with caustic. The waste is then pumped into the ocean.

b. Vapors

#11 vents to atmosphere, with the same precautions as described under Hydrazines - General.

#33 pressurizes vapors with nitrogen gas and sends them through a scrubber as described under Hydrazines - General (not the same unit, of course) and thence to the system of holding ponds previously described.

#34, #89, and #90 vent vapors through propane burners.

#36 captures N_2O_4 vapors by sparging through water drums. The contaminated water is then shipped to the NASA facility at White Sands, N. M., for disposal.

6. Inhibited Red Fuming Nitric Acid (IRFNA)

a. Liquid

#9 dilutes with water and then neutralizes with sodium carbonate.

#11 same treatment as N_2O_4.

#29 same treatment as hydrazines and N_2O_4, except that water scrubbing of the combustion gases is needed for removal of HF emissions.

#47 neutralizes spills from leaking rocket motors using a suitable alkaline.

#82 has in the past absorbed and neutralized small quantities in an alkaline solution, with the spent solution being discarded to the drainage system.

7. General Remarks on NO_2 Emissions

a. Control of NO_2 emissions are linked to the control of NO_x emissions. The NO_x compounds are generally nitric oxide (NO), nitrogen dioxide (NO_2), nitrogen tetroxide (N_2O_4) and nitrous oxide (N_2O). N_2O_4 breaks down to NO_2 under atmospheric pressure and temperature, and N_2O is not a common atmospheric pollutant. The main pollutants are NO and NO_2.

We are concerned with the control of NO_x emissions generally during all combustion processes. NO_x compounds are formed by excess oxygen

combining with atmospheric nitrogen at increased reaction temperatures during combustion. A second source of NO_x is nitrogen in the fuel. This source can be eliminated by using relatively light fuels such as natural gas.

b. Thermal Research and Engineering Corp. has discussed a number of methods used to control NO_x emissions during combustion processes. An equilibrium burner with good internal recirculation characteristics produces low NO_x levels because the mixing at equilibrium leaves little oxygen for nitrogen fixation. Another technique uses two stage combustion. The fuel is burned with less than theoretical air in the primary stage. Air is injected into the second stage to burn the remainder of fuel. A third procedure is flue gas recirculation. The gas at the end of combustion is recirculated into the combustion chamber. The result is lower flame temperatures and oxygen concentrations because of dilution with relatively inert gas. This treatment is not generally used for low NO_x concentrations. For low concentrations magnesium hydroxide scrubbing is promising. Also sulfuric acid scrubbing or ammonia reduction and scrubbing is a possibility.

Water injection has been tried experimentally. Water or low temperature steam is injected into the combustion zone reducing the flame temperature without additional oxygen. Platinum or palladium catalysts in conjunction with excess fuel helps lower NO_x emissions. This process is temperature limited to below 1500° F.

c. Tri-Mer Corp. has proposed two systems for control of NO_x emissions. One system controls NO_x emissions of 500 ppm or less and the other 500 to 5000 ppm emissions. The NO_x emissions pass through a process tank of 30 - 50% HNO_3 and a fan or gravity separator. The wastes are then filtered. Gas emissions are filtered before returning to the atmosphere and sludges or waste waters are drained.

8. Brief Discussion of Disposal at the Western Test Range

The Western Test Range includes operations of the U.S. Air Force, NASA, and a number of private companies. Furthermore, there is no one company with an overall facilities responsibility analogous to the Pan American World Airways function at the Eastern Test Range. The propellant disposal situation there is therefore rather complex and difficult in some ways to pin down. This section

is an attempt to present the situation, as we now understand it, as briefly and clearly as possible.

One of the companies at WTR wrote us that they do "not have direct responsibility for disposing of hypergolic propellants ... This responsibility is borne by ... NASA Western Launch Operations." A second company stated that the propellants are "U.S. Air Force property, and any waste or surplus is returned to the Air Force for their disposal." A third company disposes of its own residuals in quantities of less than 30 gallons. N_2O_4 is vented through a propane burner, and hydrazines are vented directly to atmosphere if plume predictions are satisfactory. The burner is used only if there is a minimum 3 knot wind in case of flame-out. Liquid hydrazines are disposed of by diluting 3 - 5 to 1, dumping in a water pit, and detoxifying (neutralizing) with a 16% solution of sodium hypochlorite. Each pad has a holding tank, and it is possible to burn up to 2 gallons at a time, although this has not been done in many years. Quantities of greater than 30 gallons should be taken by tanker to the U.S.A.F. for disposal, but this course of action has not been necessary.

NASA uses a water scrubber for Aerozine 50, and a chemical (baking soda) scrubber for N_2O_4. The Air Force is building an aeration pond.

There was also some mention of fuels being returned to the local vendor, and of unsuccessful attempts to get an oil-field disposal company to handle the waste propellants. There is also a burn pit available at the base, but it is unused. Waste oxidizer storage tanks are available at one of the old Titan II sites. One of the companies at WTR was reported to be using a scrubber for disposal, but that has not been confirmed.

B-IV: POSSIBILITES FOR RETURNING CONTAMINATED PROPELLANTS TO THE MANUFACTURER FOR REWORK

A few manufacturers stated that there might be limited possibilities for recycling contaminated propellants. Hercules Inc. wrote that "We could possibly rework N_2O_4 to reduce water content and adjust oxides content. Some contaminants, however, may not be acceptable in our plant. Each rework would probably require prior submission of an analysis showing impurities and a sample for our verification." They further stated that IRFNA reprocessing would be impossible because of the hydrofluoric acid.

Similarly, PPG Industries expressed possible interest in reworking hydrogen peroxide, and Fairmount Chemical Co., Inc. is interested in purchasing N_2H_4 "unmixed with other compounds."

B - V SPECIALIZED EQUIPMENT AND OTHER SOLUTIONS

Of the many incinerators now on the market, at least a few seem suitable for propellant disposal. Two have seen considerable use for this purpose already. One, designed by Thermal Research and Engineering Corp., of Conshohocken, Pa., has been in use at Cape Canaveral over a decade and still seems to be giving very satisfactory performance; it has been used for aqueous solutions of hydrazines and N_2O_4, and for hydrocarbon fuels. Thermal has not designed any other incinerators for this purpose since then, but is still active in burner design and emissions control. Another incinerator, built by Hirt Combustion Engineers of Montebello, California, in 1968 for one of the companies we contacted, is still in active use for disposing of aqueous solutions containing hydrazines, and has also been used for hydrocarbon fuels and exhaust gas. In addition to these, the Marquardt Company of Van Nuys, California markets commercial fume incinerators and liquid incinerators which are an outgrowth of their work in the combustion field, and have run tests on disposal of N_2H_4, UDMH, and N_2O_4 in their Sudden Expansion (SUE) incinerator. More detailed descriptions and evaluation of all these incinerators will be presented in the Interim Report covering Phase II, the evaluation phase of the study.

A related development, by Martin-Marietta Corp., Denver, Colorado, is a propane fueled, orificed circular burner. This is more a flare stack than an incinerator, and has only been used for N_2O_4 vapors, although it could probably be modified to handle hydrazine vapors. TRW Systems, Redondo Beach, California suggested "consideration of the concept of burning the propellants in a work horse engine. Such a capability is available at TRW although it has not been used specifically for disposal of propellants."

TRW also commented that filtration through a simple filter screen or strainer is often successful in removing suspended particulate matter and returning propellants to specification.

Shell Development Company's Chemical Research Laboratory in Houston, Texas, commented that "Although one of our customers in West Germany has indicated that they successfully used Shell 405 Catalyst to remove traces of hydrazine from organic process streams, we do not consider its use for disposal purposes as economical (the catalyst currently sells for $2950.00 per pound and is subject to poisoning by chemical impurities)."

The use of H_2O_2 in sewage treatment was described by Du Pont in the article mentioned in the Literature Survey, Section II - C.

The H_2O_2 provides an additional form of oxygenation or aeration to satisfy metabolistic requirements of micro-organisms. The reactions are:

(1) $2H_2O_2 \rightarrow O_2 + 2H_2O$

(2) Organics + $O_2 \xrightarrow{\text{bacteria}}$ $CO_2 + H_2O$ + bacteria sludge

The H_2O would be especially effective during periods of mechanical failures or overloads.

Allied Chemical Corp., Solvay, New York, recommended the following procedure for the disposal of IRFNA: "Unwanted material may be disposed of by addition to a large volume of water containing an alkali such as caustic soda or soda ash to neutralize the acid and calcium chloride to precipitate the fluoride. The mixture should be settled and checked to be sure the pH is 7 or higher before decanting to waste. The sludge should be taken to a landfill area for disposal."

Fisons Ltd. of Harston, Cambridge, England, a hydrazine manufacturer, recommended the following reactions for disposal of concentrated hydrazine solutions:

(1) With alkaline H_2O_2 in the presence of iron or copper (II) salts.

$$N_2H_4 + H_2O_2 \rightarrow N_2 + 4H_2O$$

(2) With excess sodium hypochlorite

$$N_2H_4 + 2NaOCl \rightarrow 2NaCl + 2H_2O$$

(3) With atmospheric oxygen in the presence of copper (II) salts.

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

CHEMISTRY OF HYPERGOLIC PROPELLANT DISPOSAL SYSTEMS

Addendum to Phase I Interim Report

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Publication of this document does not constitute National Aeronautics and Space Administration endorsement of the findings or conclusions of the report.

FOREWORD

This report was prepared by Florida Institute of Technology as an addendum to the Phase I Interim Report, by Thomas E. Bowman and Robert W. Newman, dated 28 December 1973. Its purpose is to present the chemical aspects of hypergolic propellant disposal in greater detail. This information is also being used as a basis for the work being done in Phase II, Evaluation of Current Disposal Methods.

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I. DISPOSAL OF HYDRAZINE TYPES

A. Introduction

In the following section equations are given for the chemical reactions occurring in each disposal method. Generally, the reactions presented for hydrazine will apply to UDMH and MMH with only minor modification for the methyl radical.

Many equations are simple and very obvious to a chemist but are included for completeness in spite of numerous repetitions.

B. Incineration

1. With Auxiliary Fuel

$$N_2H_4 + C_3H_8 + \overbrace{6O_2 + 6(3.76)N_2}^{\text{Air}} \longrightarrow 6(3.76)N_2 + 3CO_2 + 6H_2O + O_2 + \underset{\text{excess}}{}$$

traces * of $H_2 + NO_x + CO + N_2H_4 + HC + NH_3$

* Notes: (Figures are from actual analysis. Refer to Table 2 in Section VI for detailed data.)

1. H_2 , from 2 ppm to 2.5% or more.
2. NO_x , from 2 ppm to 4,000 ppm.
3. CO , from 2 ppm to 5% or more.
4. N_2H_4 , from 0.1 ppm to 2 ppm.
5. HC , 5 - 10 ppm to several %.
6. NH_3 or Amine, 1 - 5 ppm to 400 ppm.

2. "SUE" Incinerator (Marquardt Co.)

Over-stoichiometric burning of liquid hydrazine with auxiliary fuel followed by water-quench to 2000°F and reburning of combustion gases to eliminate $CO + H_2$.

UDMH propellant:

$$(CH_3)_2\ N_2H_2 + 3O_2 \longrightarrow N_2 + 3H_2O + 2CO + H_2 + \underset{\text{trace}}{NO_x}$$

Propane:

$$C_3H_8 + 4O_2 \longrightarrow CO_2 + 2CO + 4H_2O$$

$$N_2 + 7H_2O + CO_2 + 4CO + H_2 + \underset{\text{trace}}{NO_x}$$

Reburning Combustible Gases:

$$4CO + H_2 + 2\ 1/2\ O_2 \longrightarrow 4CO_2 + H_2O$$

Notes:

1. "SUE" Incinerator emission levels reported by Marquardt as low as 2 ppm NO.

2. Incinerators used in USAF - sponsored test program burn up to 16.5 lbm/minute waste liquid propellants. Effluents limited to $\frac{.03 \text{ lbs}}{\text{min.}}$ NO_x.

3. Open Pit Burning

$$N_2H_4 + O_2\ (Air) \longrightarrow N_2 + 2H_2O + \overset{\text{traces}}{NO_x}$$

C. Chemical Treatments (Neutralization)

Equations show reactions in dilute solutions.

$$1.\quad N_2H_4 + 2H_2O_2 \xrightarrow[\text{Cat.}]{\text{Cu++}} N_2 + 4H_2O$$

In basic solution N_2H_4 acts as a reducing agent:

Possible 1/2 reactions

$$\longrightarrow N_2 + 4H_2O + 4e$$

$$\longrightarrow NH_3 + 1/2N_2 + H_2O + e$$

$$\longrightarrow 1/2N_3^- + 1/2\ NH_3 + \frac{5}{2}\ H_2O + 2e$$

$$2.\quad N_2H_4 + Ca\ (ClO)_2 \longrightarrow N_2 + H_2O + 2\ HCl + CaO$$

In solution CaO reacts:

$$CaO + 2\ HCl \longrightarrow Ca\ Cl_2 + H_2O$$

$$CaO + H_2O \longrightarrow Ca\ (OH)_2$$

$$3.\quad N_2H_4 + 2\ NaOCl \longrightarrow N_2 + 2H_2O + 2NaCl$$

$$4.\quad N_2H_4 + HCl \longrightarrow N_2H_5^+ + Cl^-$$

Possible 1/2 reactions in acidic solution

$$\longrightarrow N_2 + 5H^+ + 4e$$

$$\longrightarrow 1/2\ N_2 + NH_4^+ + H^+ + e$$

$$\longrightarrow 1/2\ NH_3 + 1/2\ NH_4^+ + \frac{5}{2}H^+ + 2e$$

$$5.\quad N_2H_4 + N_2O_4 \longrightarrow N_2 + 2NO + 2H_2O$$

D. Catalytic Decomposition

1. Al_2O_3 coated with certain metals or metal oxides.

$$N_2H_4 \xrightarrow{\text{Cat.}} 1/2\ N_2 + 1/2\ H_2 + NH_3$$

Details of reaction found in classified literature.
Catalyst is generally expensive.

2. $$N_2H_4 + O_2 \xrightarrow{Cu^{++}} N_2 + 2H_2O$$

O_2 is supplied by bubbling air into solution. Reaction is fairly slow at ambient temperature, but increases with rise in temperature.

3. General Equation:

$$N_2H_4 + \begin{matrix}\text{Metal}\\ \text{Catalyst}\end{matrix} \xrightarrow{\Delta} \begin{cases} N_2 + NH_3 & (1) \\ N_2 + H_2 & (2) \\ N_2 + NH_3 + H_2 & (3) \end{cases}$$

Balanced Equations:

$$3N_2H_4 \xrightarrow[\text{Cat.}]{\Delta} N_2 + 4NH_3 \quad (1)$$

$$N_2H_4 \xrightarrow[\text{Cat.}]{\Delta} 2H_2 + N_2 \quad (2)$$

$$2N_2H_4 \xrightarrow[\text{Cat.}]{\Delta} N_2 + H_2 + 2NH_3 \quad (3)$$

E. Dilution

1. $$N_2H_4 + H_2O \xrightarrow{\text{Copious}} \underset{\text{Dilute Solution}}{HNO_3 + HNO_2} \xrightarrow[\text{Air Oxidation \& Bacterial Action in Holding Ponds}]{} N_2 + NH_3 + H_2O$$

Rewritten:

$$2N_2H_4 \xrightarrow{\text{Bacteria \& Air}} N_2 + 2NH_3 + H_2O$$

2. $$N_2H_4 + O_2 \xrightarrow{\text{Air Bubbling}} 2\ H_2O + N_2$$

Aeration reaction is slow at room temperature.

F. Hydrazine Vapor Scrubbing

1. With H_2O

a.) $N_2H_4 + H_2O \longrightarrow$ Solution of N_2H_4 and NO_x

b.) $N_2H_4 \cdot (CH_3)_2 N_2H_2 + H_2O \longrightarrow$ Solution of N_2H_4, UDMH, NO_x

c.) $CH_3 N_2H_3 + H_2O \longrightarrow$ Solution of MMH + NO_x

Scrubber liquor discharged to holding pond or further chemical treatment as shown in Section C.

G. Atmospheric Venting (Evaporation)

1. $N_2H_4 \longrightarrow$ Mixture of gases evolved to atmosphere containing vapors of NO, NO_2, N_2H_4

2. UDMH $\longrightarrow$ Mixture of gases containing NO, NO_2, UDMH

3. MMH $\longrightarrow$ Mixture of gases containing NO, NO_2, MMH

II. DISPOSAL OF NITROGEN TETROXIDE

A. Incineration - Liquid

$$N_2O_4 + \overset{\text{Auxiliary}}{\text{FUEL}} + \text{AIR} \longrightarrow N_2 + CO_2 + H_2O + (H_2 + CO + NO_x + N_2O_4)\ *$$

*Notes:
- H_2 from traces up to over 4×10^5 ppm. At stoichiometric propane/ N_2O_4 ratio $\sim 4 \times 10^4$ ppm.
- CO from traces up to over 3.5×10^5 ppm. At stoichiometric propane/ N_2O_4 ratio $\sim 1.4 \times 10^5$ ppm.
- NO + NO_2 from traces up to over 20,000 ppm. At stoichiometric propane/ N_2O_4 ratio $\sim 1.5 \times 10^4$ ppm.
- N_2O_4 present in oxidizer - rich runs.

Combustion, particularly at high temperatures, slowly converts atmospheric N_2 to NO. This NO is oxidized, either slowly by O_2 or rapidly by O_3, to produce NO_2.

NASA TND 3965 reported no detectable NO_x utilizing a 'flare' type burner when operated in a slightly fuel rich mode.

Operation of incinerator at very lean $\frac{\text{FUEL}}{N_2O_4}$ ratio ($< .02$) with very high $\frac{\text{AIR}}{\text{FUEL}}$ ratio (> 20) is not feasible due to the low temperature and consequent abundant NO_x gas release into the atmosphere. For this reason, under-stoichiometric burning with N_2O_4 and AIR is not considered practical.

Operation at over-stoichiometric incineration $\left(\frac{\text{FUEL}}{N_2O_4} > 0.4\right)$ and with relatively high $\frac{\text{FUEL}}{\text{AIR}}$ ratio and higher temperature is more desirable. Under these conditions more FUEL is used and more CO and H_2 generated but the amount of NO_x formed is considerably reduced.

B. Neutralization *

The first step in reactions 1-5 shown below is:

---

* Disposal of large quantities of liquid N_2O_4 by neutralization reactions is expensive.

$$N_2O_4 + H_2O \xrightarrow{\text{Copious}} \text{Solutions of } HNO_3 \text{ and } HNO_2$$

The second step is metathesis reaction in solutions:

1. $HNO_3 + HNO_2 + 2Na\,H\,CO_3 \longrightarrow$ Solution of $Na\,NO_3 + Na\,NO_2 + 2H_2O + 2CO_2\uparrow$

2. $HNO_3 + HNO_2 + Na_2\,CO_3 \longrightarrow$ Solution of $Na\,NO_3 + Na\,NO_2 + H_2O + CO_2\uparrow$

3. $HNO_3 + HNO_2 + 2Ca\,(OH)_2 \longrightarrow$ Solution of $Ca\,(NO_3)_2 + Ca\,(NO_2)_2 + 2H_2O$

4.* $HNO_3 + HNO_2 + 2Na\,OH \longrightarrow$ Solution of $Na\,NO_3 + Na\,NO_2 + 2H_2O$

5. $HNO_3 + HNO_2 + Mg\,(OH)_2 \longrightarrow$ Solution of $Mg\,(NO_3)_2 + Mg\,(NO_2)_2 + H_2O$

6. $N_2O_4 + \underset{\text{Urea}}{(NH)_2\,CO} \longrightarrow NH_4\,NO_3 + CO_2\uparrow + N_2\uparrow$

NO_2 reacts differently in hot H_2O than in cold H_2O :

a.) With hot H_2O :

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

This is an oxidation-reduction reaction in which the dioxide is both the oxidizing and the reducing agent.

b.) With cold H_2O :

$$2\,NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

Disposal of small quantities of N_2O_4 by evaporation to the atmosphere is acceptable. Incineration is recommended for large quantities, i.e. > drum lots.

C. Incineration - Vapors

1. At 200°C :

$$N_2O_4 \xrightarrow{\Delta} 2NO_2 + \underset{\text{trace}}{NO}$$

---

* PAN-AM method for oxidizer concentrations < 5 % used at CKAFS.

2. Dissociation reactions at 2000 °C or higher:

   a.) Under oxidizing conditions:

   $$2NO_2 \xrightarrow{\Delta} 2NO + O_2$$

   b.) Under strongly reducing conditions:

   $$2NO_2 \xrightarrow{\Delta} N_2 + 2O_2$$

3. Theoretical equation under strongly reducing conditions -

   High $\frac{FUEL}{AIR}$ and high $\frac{FUEL}{N_2O_4}$ Ratios:

   $$5N_2O_4 + 2C_3H_8 \longrightarrow 6CO_2 + 5N_2 + 8H_2O$$

NASA TN D - 3965: Analysis of combustion products from a 'flare' type burner showed no detectable quantity of NO_x when reducing conditions prevaled, but NO_x was present if burner operated with an oxidizer - rich feed (oxidizing conditions).

D. Scrubbing N_2O_4 Vapors

Liquid evaporated: $N_2O_4 \longrightarrow 2NO_2$ (mostly)

1. When vapors absorbed in plain H_2O :

   $$2NO_2 + H_2O \xrightarrow{\text{spray}} \text{Solution of } HNO_3 + HNO_2$$

2. When vapor absorbed in bicarbonate solution:

   $$2Na\,H\,CO_3 + HNO_3 + HNO_2 \longrightarrow Na\,NO_2 + Na\,NO_3 + H_2O + CO_2\uparrow$$

NOTE: NO_2 vapors are relatively difficult to capture in H_2O.

E. Venting to Atmosphere

$N_2O_4 \longrightarrow 2NO_2 \longrightarrow$ Air Dilution and Dissipation

Vapors mostly

Secondary reactions of NO_2 vapors with atmospheric moisture:

$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO\uparrow$$

Also:

$$NO + 1/2\ O_2 \longrightarrow NO_2$$

Notes:

1. NO_2 is a pollutant and aids in forming smog.
2. The oxidation of NO to NO_2 is rapid at high concentrations in air, but it is slow at low concentrations except in the presence of hydrocarbons and sunlight.

III. DISPOSAL OF INHIBITED RED FUMING NITRIC ACID

A. Incineration

(Inhib.) $2\,HNO_3 + FUEL \xrightarrow{\Delta} N_2 + \overset{trace}{NO_x} + H_2O + O_2 + HF +$ Fuel Combustion Products (CO_2, CO, H_2O, etc.)

B. Neutralization

Soda ash - slaked lime solution is commonly used for neutralizing IRFNA. The contained inhibitor (1% HF) is precipitated as CaF_2 and may be filtered off. The neutral solution of Na NO_3 is diluted with H_2O and discharged.

Equations:

1. $2\,HNO_3 + Na_2\,CO_3 \longrightarrow 2\,Na\,NO_3 + CO_2\uparrow + H_2O$

   $2\,HF + Ca\,(OH)_2 \longrightarrow CaF_2\downarrow + 2H_2O$

   Filter, to Solid Waste Disposal

2. $HNO_3 + Na\,OH \longrightarrow Na\,NO_3 + H_2O$

3. $HNO_3 + NH_4OH \longrightarrow NH_4\,NO_3 + H_2O$

C. Vapors of IRFNA

1. Vent Through Burner :

   $2\,HNO_3 \xrightarrow{\Delta} N_2 + NO_x + H_2O + O_2$

2. Scrubbing :

   a.) With H_2O :

   $HNO_3\ /\ NO\ /\ NO_2 + \overset{copious}{H_2O} \longrightarrow$ Dilute Solution of $HNO_3\ /\ HNO_2$

   b.) With Na H CO_3 Solution:

   HNO_3 or $NO_x + Na\,H\,CO_3 \longrightarrow Na\,NO_3 + Na\,NO_2 + CO_2 + H_2O$

3. Vent to Atmosphere

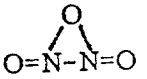
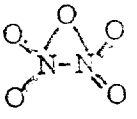
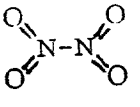
HNO_3 or NO_x $\longrightarrow$ HNO_3 + NO_x Vapors
Diluted with Copious Air

D. Dilution

HNO_3 + copious H_2O $\longrightarrow$ Dilute Solution of HNO_3
Concentrated
Neutralized or Discharged to Ground Surface or Stream

TABLE 1

OXIDES OF NITROGEN

#	Name	Formula	N_2 Valence	Structure	Solubility in H_2O Cold	Solubility in H_2O Hot	Remarks
1.	Nitric Oxide	NO	2	N=O	$\frac{7.3\text{ cc}}{100\text{ ml}}$ H_2O@0°C	$\frac{2.4\text{ cc}}{100\text{ ml}}$ H_2O@60°C	Common air pollutant
2.	Nitrous Oxide	N_2O	3		$\frac{130\text{ cc}}{100\text{ ml}}$ H_2O@0°C	$\frac{51\text{ cc}}{100\text{ ml}}$ H_2O@25°C	Relatively inactive in air or with O_3. Not a pollutant.
3.	Dinitrogen Trioxide (Nitrous Anhydride)	N_2O_3	4		Sol. Cold H_2O	Dissoc. in Hot H_2O	Unstable
4.	Dinitrogen Pentoxide (Nitric Anhydride)	N_2O_5	6		Sol. Cold H_2O	Dissoc. to HNO_3 in Hot H_2O	Unstable
5.	Nitrogen Dioxide	NO_2	4	O=N=O	Sol. in Alk., Chloroform	CS_2,	Common air pollutant
6.	Dinitrogen Tetroxide	N_2O_4	5		Sol.		A dimer of NO_2. An equilibrium mixture of N_2O_4 and NO_2 (84%) (16%) @20°C

IV. DISPOSAL OF HYDROGEN PEROXIDE

A. Chemical Disposal

1. $H_2O_2 \longrightarrow H_2O + 1/2\ O_2$

2. Catalytic

$$H_2O_2 \xrightarrow[\text{Pt or Ag Cat.}]{\substack{212^\circ F \\ .5\text{-}1\%\ Na\ OH}} H_2O + O \longrightarrow H_2O + 1/2\ O_2$$

B. Biological Disposal

Very Dilute $H_2O_2 \longrightarrow H_2O + 1/2\ O_2$ Discharged to Pond or Stream

$$\text{Nutrients} + \text{D.O.} \xrightarrow{\text{Micro Organisms}} CO_2 + H_2O + \text{Bacterial Sludge}$$

NOTE: Waste H_2O_2 presents the least disposal problem of any of the materials under study and presents no pollution problems.

V. VARIABLES AFFECTING DISPOSAL METHODS

A. Introduction

Incineration is a controlled combustion process to convert the waste propellant to a less toxic, less bulky, less noxious or more easily disposable material. The principal undesirable incineration products from an environmental view point are NO_x and CO. Occasionally, NH_3 or hydrocarbons or soot are released when operating under non-optimum conditions. Direct flame or catalytic destruction of waste propellants produce an effluent of N_2, CO_2 and H_2O vapor which can be vented safely to the atmosphere. Undesirable compounds (such as NO_x) formed during incineration may require a secondary treatment, such as scrubbing, to lower their concentration to acceptable levels prior to atmospheric release.

Important criteria for an adequate disposal system of a waste propellant include the following:

1.) The effluent should be inconspicuous and safe.
2.) The system should not be prohibitively expensive to operate and maintain.
3.) It must meet pollution standards.

Gas sampling techniques and analysis must be adequate to provide meaningful data. Factors to be considered are:

1.) The sample must be representative.
2.) The integrity of the sample must be preserved.
3.) Initial cost and operating cost of equipment.
4.) The possibility of biased interpretation and/or omissions of test results in reports.

B. Incinerator Variables

The variables which have the greatest effect on the completion of the oxidation of the propellant waste are:

1.) Combustibility
2.) Reaction Temperature
3.) Residence Time in Incinerator
4.) Gas Turbulence in Reaction Zone.

Hydrazine, UDMH, and MMH have low flammability limits. N_2O_4 and IRFNA decompose relatively easily and support combustion. With proper feed rates and the use of auxiliary fuels combustibility is readily controllable.

Temperature can be controlled over some range * by varying the $\frac{AIR}{FUEL}$ ratio.

Economic considerations are paramount in the selection of incineration systems because of the high auxiliary fuel cost. A minimum temperature must be maintained for satisfactory decomposition of wastes. An upper temperature limit is dictated by the lifetime of the refractory lining.

Rates of oxidation reactions are increased rapidly by higher temperatures. A design range of 2400° F to 3000° F or higher may be specified depending upon the waste propellant being disposed. Three basic methods of controlling the combustion temperature are:

1.) Excess Air Control
2.) Two Stage Combustion
3.) H_2O Injection.

Sufficient time must be provided during the waste incineration to allow droplets or particles to react with O_2 or oxidizers. From 0.1 to 1 second or more may be required. The evaluation of this time factor can only be made by tests of individual incinerators or manufacturers' recommendations followed.

The degree of turbulence in the reaction zone significantly affects the incinerator performance. Intimate mixing of the air and waste propellant gases is required for completeness of combustion. Ideally, adequate destruction of waste propellant is to reduce N_2O_4 to N_2 with minimum amount NO and to oxidize the hydrazines with auxiliary fuel to H_2O, N_2, and CO_2. Effectiveness is judged by the combustion results as indicated by stack effluent analysis.

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* The range is very dependent on the basic incinerator design.

C. NO Formation

NO is a pollutant common to incineration processes which utilize air. NO formation results from O_2 and N_2 reacting at the elevated temperature. Figure 1 presents graphically the thermodynamic equilibrium concentration of NO as a function of % excess air at various reaction temperatures for combustion of materials that do not contain nitrogen themselves. The incineration of waste propellants would be expected to yield higher values than shown because all materials under study are high-percentage nitrogen containing compounds (except H_2O_2 which is not incinerated).

To reduce NO amount in exhaust gases from N_2O_4 destruction, over-stoichiometric incineration with relatively low AIR-FUEL ratio ($<.04$) and higher temperature is utilized. Under these conditions more fuel is used and more CO and H_2 generated but with lesser amounts of NO appearing in the stack gas analysis due to the dilution effect of excess air. Further, the feed rate of N_2O_4 to the incinerator is usually less than for N_2H_4 resulting in additional dilution effects.

Although adding considerable to operating costs, the auxiliary hydrocarbon fuels act as reducing agents and will decrease NO concentrations to lower levels. A high conversion efficiency is of primary concern as opposed to economic considerations when handling hazardous wastes.

D. Flare Burner

The 'flare' type burner, as designed by Martin Marietta Corp., consists basically of a cylinder (one standard configuration is 8" diameter by 3' long) containing a plenum in which propane and waste N_2O_4 vapors are injected, and a burner head. A wind shroud protects the head from flame out. A continuous pilot is provided at the top of the burner head to ignite the gas mixture. Approximately 10 pounds per minute of N_2O_4 can be destroyed in the case of the 8 inch configuration. Essentially, the brown NO_2 vapors from N_2O_4 are reduced to N_2 and a small amount of NO, which are colorless (and therefore invisible) gases.

Flares are affected by atmospheric conditions, especially strong winds. They are not considered infallible because unburned gases may escape from a flare system. They are expedient and economical for high-volume discharge of combustible waste gases.

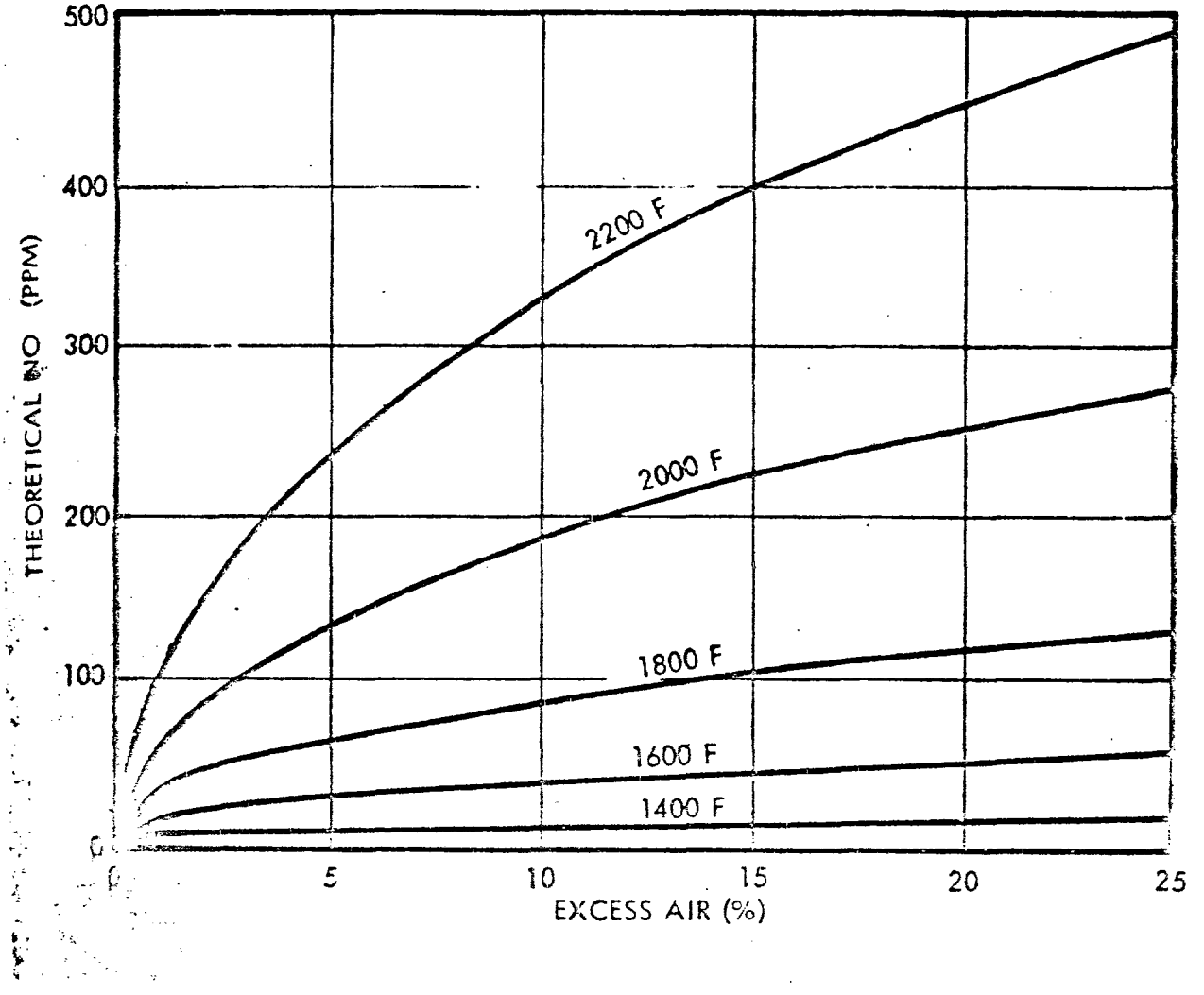

Figure 1. Equilibrium NO Concentrations in Combustion Effluents

(R. D. Ross, Industrial Waste Disposal, Van Nostrand - Reinhold Corp., N. Y., 1968, p. 340; Quoted by R. S. Ottinger et al, TRW Report No. 21485-6013-RU-00, 1973.)

E. Open Pit Incineration

An open pit incinerator consists of a rigid shell of suitable width and height with an open top. An array of closely spaced nozzles might be used to provide high velocity air over the burning zone.

High burning rates, long residence time, and high flame temperature are achieved. Smoke can be controlled but some particulate matter (soot) and a visible plume of toxic gas (NO_2) is produced. Exit gases are released directly to the atmosphere.

F. Open Incineration

Open incineration is the burning of waste material on open land without the use of combustion equipment. This method is not used frequently for propellant destruction. Generally, considerable black smoke along with NO_x and CO are evolved to the atmosphere. These emissions are the result of uncontrolled combustion temperature, incomplete combustion due to poor gas mixing with air, and insufficient residence time of the generated particulate at elevated temperature.

Open burning is not considered to be an adequate form of waste propellant disposal because of associated loss of gaseous effluent control.

VI. PRELIMINARY EVALUATION DATA

A. Introduction

In this section a collection of analytical data in tabular form is presented and brief comments are made on the methods for destroying the waste propellants. Insufficient analytical data are available at this time on the composition of stack emissions to permit making a comparative evaluation of the various incinerators or to discuss the merits of the different disposal methods.

B. Comments on Methods for Destroying Propellants

The major products during incineration of hydrazine - type wastes with auxiliary fuels are N_2 , H_2O , CO_2 , CO formed in varying concentrations depending on thermal and concentration parameters as well as other factors. Minor products of combustion are H_2 , NO_x , C , SO_2 and hydrocarbons. The concentration of NO_x is of prime interest from the environmental and ecological viewpoints.

Table 2, compiled from available analytical reports *, shows the high and low concentration of combustion products from incineration of N_2H_4 , UDMH and N_2O_4. A study of these reports shows that under optimum conditions only small quantities (5 - 500 ppm) of NO_x pollutant are formed, but up to 10 or 20 times these amounts can form under non-optimum conditions. It also became obvious that the same equipment operating under varying stoichiometric ratio, temperature, propellant concentration or type, feed rate or other parameters will produce a wide compositional range of the gaseous constituents.

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* Compilation of data was from the following reports:

a.) Pan Am U327, 3 January 1972

b.) Pan Am MD-EH, 26 February 1971

c.) Pan Am, 8 October 1970

d.) Joel E. Hutson, "Toxic Waste Burner Evaluation". Final Report, AFRPL Contract No. F04611-73-C-0007 (Marquardt Co. Report S-1271), November 1973.

TABLE 2

CONCENTRATION OF COMBUSTION PRODUCTS

Combustion Product	Incineration of:					
	N_2H_4		UDMH		N_2O_4	
	Low	High	Low	High	Low	High
NO_x, ppm	2	3720	20	4113	250	7990
CO, ppm or %	5 ppm	1.9%	2 ppm	7.6%	1 ppm	7.5%
CO_2, %	0.3%	4.4	0.3	9.1	8.3	16.7
O_2, %	0.5%	18	0.2	20.6	4.6	7.9
H_2, ppm or %	N.D.	N.D.	.89%	12.4%	N.D.	N.D.
Total HC, ppm	8	N.D.	9.5	1750	4	40.1
HC (As Ci), ppm	< 5	50	< 10	1.07%	N.D.	N.D.
HC (As CH_4), ppm	< 5	3230	< 10	7000	23	17,010
NH_3, ppm	6	46	< 0.8	2170	N.D.	N.D.
Amines - RNH_2 ppm	< 5	50	< 4	390	N.D.	N.D.
UDMH, ppm	---	---	< 0.5	< 2.0	---	---
N_2H_4, ppm	< .02	30	---	---	---	---
N_2O_4 (As NO_2) ppm	---	---	---	---	N.D.	N.D.

N.D. = No Data.

C. Amount of Pollutants from N_2O_4 Disposal

A study of the chemistry of the destructive procedures for N_2O_4 reveals the following products are released to the environment:

Method	Pollutant	Other Products	Weight of Pollutant	Receiving Environment
1. Incineration	NO CO	H_2O, O_2, H_2, CO_2 (from auxiliary fuel)	From trace to .65 lb. NO per lb. N_2O_4 From trace to ~ .06 lb. CO per lb. aux. fuel	Air
2. Neutralization	Solutions of HNO_3 and HNO_2	Na+, Ca++ or other cations	1.8 lb. NO_3^- & NO_2^- anions per 1 lb. N_2O_4	Surface and Ground Waters
3. Atmospheric Venting	Mostly NO_2 and NO	---------	From .65 lb. to 1 lb. NO_2 and NO vapors per 1 lb N_2O_4	Air

The pollutants are either gaseous (NO , NO_2 , CO) or water soluble compounds (NO_3^- , NO_2^-).

It's evident that for every pound of N_2O_4 incinerated up to .65 lb of NO can be formed; for every pound neutralized, 1.8 lbs NO_3^- and NO_2^- anions are formed; for every pound vented, .65 to 1 lb NO and NO_2 vapors are formed. However, due to dilution effects and the reducing effects of hydrocarbon fuels the NO concentration in stack emissions is in the 10 to 10,000 ppm range.

In N_2O_4 neutralization reactions, such as occur in chemical treatment or scrubbing procedures, the combined anion weight of NO_3^- and NO_2^- is 1.8 lb for every pound of N_2O_4 treated. In an efficient system the gaseous emission to air will be minimal but the resulting highly corrosive salts formed present a secondary disposal problem. If improperly handled these salts cause deleterious effects on the surrounding area. Another disadvantage with neutralization is its inherent high cost for both the auxiliary chemicals and the initial capital investment in an efficient system for toxic gas removal.

Atmospheric venting releases between 0.65 lb to 1 lb combined weight of NO and NO_2 vapors per pound of N_2O_4 evaporated, depending on temperature and other parameters. Dissipation of these toxic vapors into a large volume of air under suitable meteorological conditions appears at first sight to be a solution to pollution. These two gases are smog-formers, however, and readily react with atmospheric moisture to form corrosive nitric and nitrous acids.

The vapor scrubbing method presents high maintenance cost and high operating cost problems per unit of N_2H_4 treated. Nozzle plugging, corrosion, and overloading are also pertinent problems to be considered.

D. Methods of Destroying IRFNA

The chemistry of IRFNA incineration is similar to that of N_2O_4 incineration. N_2 and NO_x are the gaseous end products plus small quantities of HF which may require scrubbing out and precipitation.

The neutralization method with soda ash-slaked lime or alkali results in a soluble NO_3 solution which is usually further diluted and discharged into a stream, sewer or ground surface.

Venting of vapors to atmosphere or scrubbing vapors entails capturing the vapors and dealing with dilute NO_3 solution or gaseous NO_x.

A significant difference between IRFNA and N_2O_4 in practical terms is the much higher boiling point of IRFNA. While N_2O_4 liquid can be allowed to vaporize by a slight addition of heat (or exposure to atmospheric pressure on a warm day) so that only vapor disposal methods need be used, separate liquid disposal methods are necessary in the case of IRFNA.

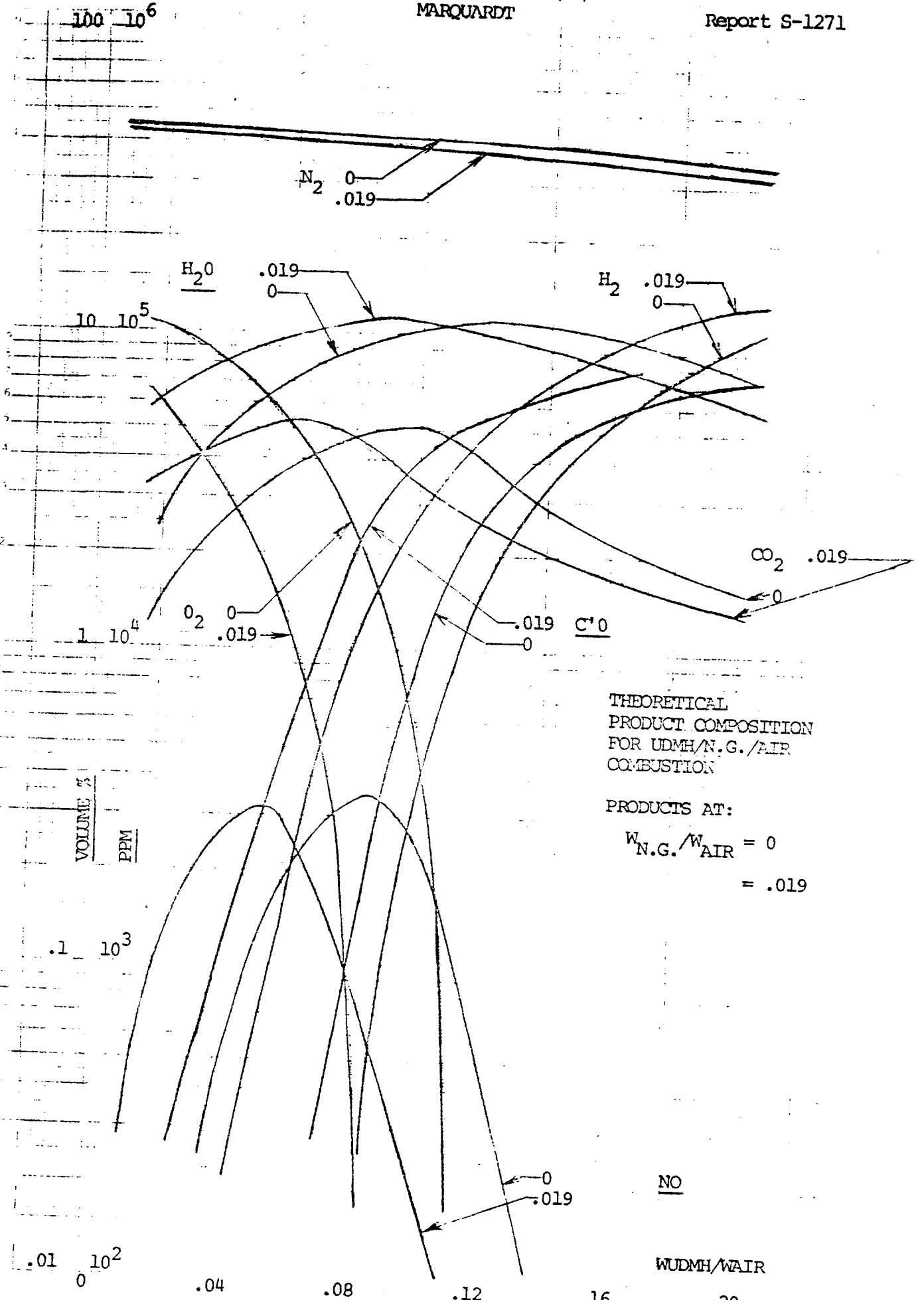
E. Theoretical Equilibrium Curves

The theoretical equilibrium compositions of the products of combustion of various combinations of UDMH, N_2H_4 , N_2O_4 , natural gas, propane, and air were computed by Marquardt Company as part of Air Force Rocket Propulsion Laboratory Contract No. FO 4611-73-C-0007. These computations were based on NASA Report SP-273, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman - Jouquet Detonations" , by Sanford Gordon and Bonnie J. McBride, 1971. The results are reproduced in Figures 2-4, as useful guidelines for future equipment evaluation.

As an example, Figure 4 indicates that in order to operate at low NO discharge concentrations, a very lean $\frac{FUEL}{N_2O_4}$ ratio is required with a large amount of dilution air. Concomitant problems, however, preclude this mode of operation due to low temperature, incomplete N_2O_4 decomposition and other negative factors.

Conversely, Figure 4 also indicates that satisfactory operation can be obtained at over-stoichiometric conditions with little excess air present. Thus, decreasing amounts of air create decreasing amounts of NO. The over-stoichiometric regime was considered the more desirable alternative.

Finally, Table 3 compares the amounts of NO or CO formed at various AIR/ FUEL/ PROPELLANT ratios and at peak values as read from the Marquardt Theoretical Equilibrium Curves. Table 4 gives stoichiometric ratios for use in Phase II evaluations.



THEORETICAL PRODUCT COMPOSITION FOR UDMH/N.G./AIR COMBUSTION

PRODUCTS AT:

$W_{N.G.}/W_{AIR} = 0$

$= .019$

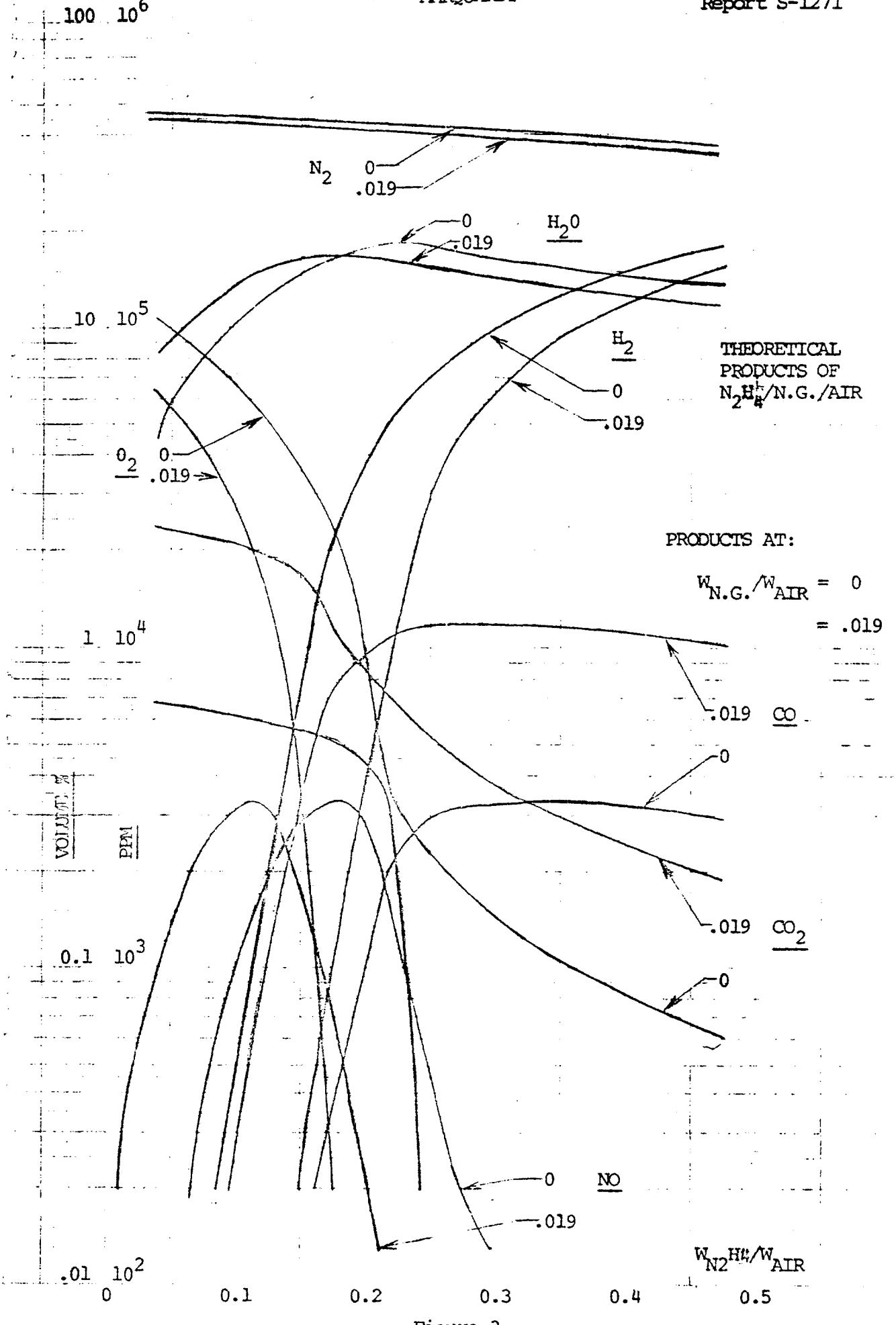

100 10^6
10 10^5
1 10^4
0.1 10^3
.01 10^2
VOLUME %
PPM
N2 0
.019
H2O
0
.019
H2
0
.019
O2
0
.019
THEORETICAL
PRODUCTS OF
N2H4/N.G./AIR
PRODUCTS AT:
WN.G./WAIR = 0
= .019
.019 CO
0
.019 CO2
0
NO
0
.019
WN2H4/WAIR
0
0.1
0.2
0.3
0.4
0.5

Figure 3.

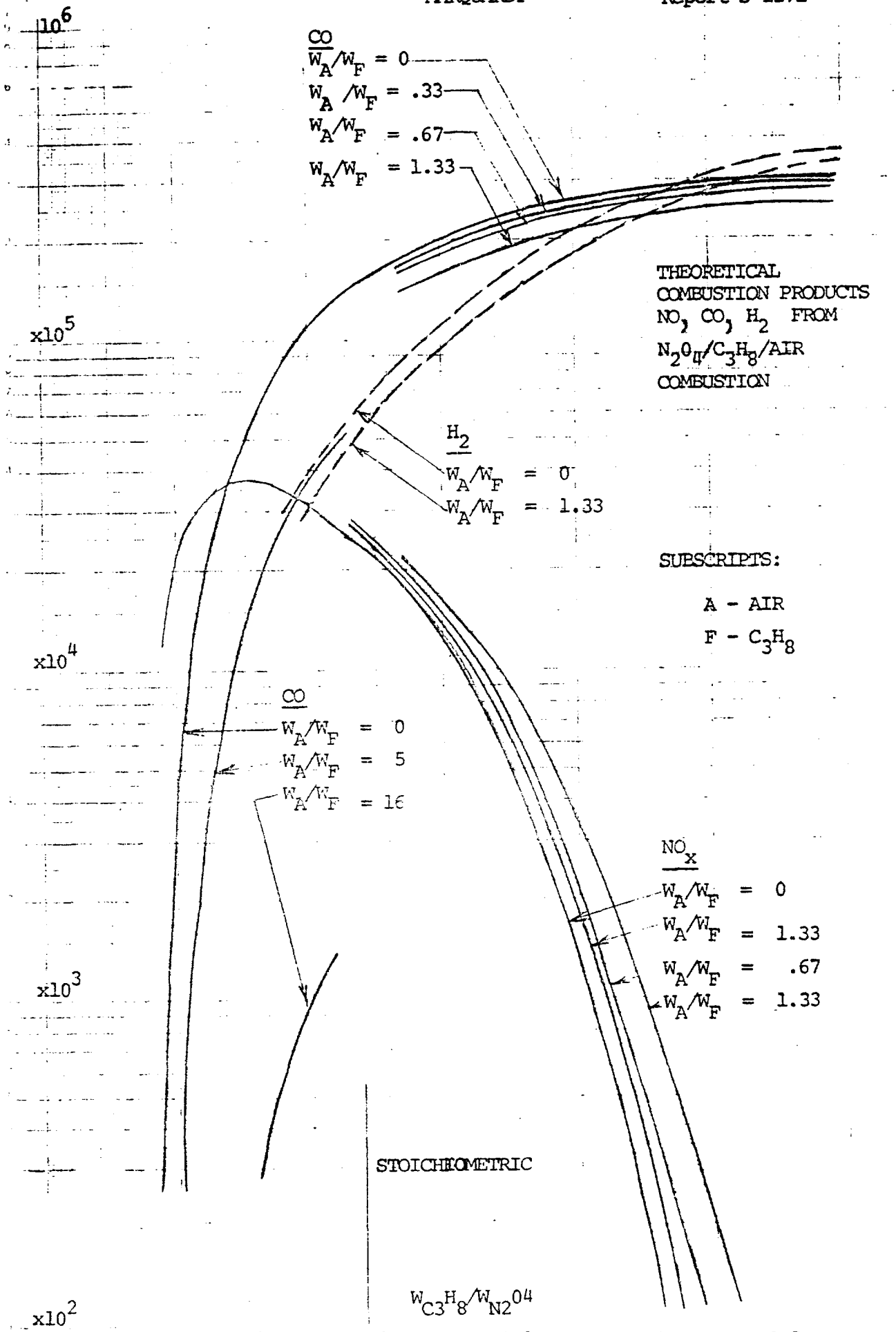

10^6
$x10^5$
$x10^4$
$x10^3$
$x10^2$
CO
W_A/W_F = 0
W_A/W_F = .33
W_A/W_F = .67
W_A/W_F = 1.33
THEORETICAL COMBUSTION PRODUCTS NO, CO, H_2 FROM N_2O_4/C_3H_8/AIR COMBUSTION
H_2
W_A/W_F = 0
W_A/W_F = 1.33
SUBSCRIPTS:
A - AIR
F - C_3H_8
CO
W_A/W_F = 0
W_A/W_F = 5
W_A/W_F = 16
NO_x
W_A/W_F = 0
W_A/W_F = 1.33
W_A/W_F = .67
W_A/W_F = 1.33
STOICHEOMETRIC
W_{C3H8}/W_{N2O4}
0.1
0.2
0.3
0.4
0.5
0.6

Figure 4.

TABLE 3

SELECTED POINTS FROM MARQUARDT THEORETICAL EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS

	Amount NO Formed		Amount CO Formed
Material Incinerated	At Stoichiometric Ratio	NO and Ratio @ NO Peak	At Stoichiometric Ratio
UDMH	$\mathcal{O}$ = .19 $\frac{W_{N.G.}}{W_{AIR}} = 0$ 3000 ppm	$\frac{W_{UDMH}}{W_{AIR}} = .09$ 4500 ppm	$\frac{W_{UDMH}}{W_{AIR}} = .19$ $\frac{W_{N.G.}}{W_{AIR}} = 0$ 13,000 ppm
	$\frac{W_{N.G.}}{W_{AIR}} = .019$ 200 ppm	$\frac{W_{UDMH}}{W_{AIR}} = .055$	$\frac{W_{N.G.}}{W_{AIR}} = .019$ 63,000 ppm
N_2H_4	$\mathcal{O}$ = .23 $\frac{W_{N.G.}}{W_{AIR}} = 0$ 2000 ppm	$\frac{W_{N_2H_4}}{W_{AIR}} = .19$ 4000 ppm	$\frac{W_{N_2H_4}}{W_{AIR}} = .23$ $\frac{W_{N.G.}}{W_{AIR}} = 0$ 2100 ppm
	$\frac{W_{N.G.}}{W_{AIR}} = .019$ 165 ppm	$\frac{W_{N_2H_4}}{W_{AIR}} = .12$ 4000 ppm	$\frac{W_{N.G.}}{W_{AIR}} = .019$ 14,000 ppm

TABLE 3 (CONTINUED)

Material Incinerated	Amount NO Formed		Amount CO Formed
	At Stoichiometric Ratio	NO and Ratio @ NO Peak	At Stoichiometric Ratio
N_2O_4	$\frac{W_{C_3H_8}}{W_{N_2O_4}} = .19$ 1600 ppm	$\frac{W_{C_3H_8}}{W_{N_2O_4}} = .11$ 2200 ppm	$\frac{W_{C_3H_8}}{W_{N_2O_4}} = .19$
		$\frac{W_{C_3H_8}}{W_{N_2O_4}} < .45$ NO < 200	$\frac{W_{AIR}}{W_{C_3H_8}} = 0$ 150,000 ppm

TABLE 4

STOICHIOMETRIC RATIOS

Propellant	$S_R = \frac{W_{PROP.}}{W_{AIR}}$	$S_R' = \frac{W_{AIR}}{W_{PROP.}}$	Comments
UDMH	.109	9.17	Without Auxiliary Fuel
N_2H_4	.232	4.32	Without Auxiliary Fuel
UDMH • N_2H_4	.0952	10.5	Without Auxiliary Fuel 50/50% Mixture
UDMH	.0842	11.9	With Auxiliary Fuel (Propane)
N_2H_4	.092	10.9	With Auxiliary Fuel (Propane)
UDMH • N_2H_4	.075	13.3	With Auxiliary Fuel (Propane)
N_2O_4	$\frac{W_{FUEL}}{W_{N_2O_4 + AIR}} = .069$	14.5 $\frac{W_{N_2O_4 + AIR}}{W_{FUEL}}$	With Auxiliary Fuel (Propane)
N_2O_4	$\frac{W_{FUEL}}{W_{N_2O_4 + AIR}} = .07$	14.3 $\frac{W_{N_2O_4 + AIR}}{W_{FUEL}}$	With CH_4 Fuel

HYPERGOLIC PROPELLANTS

LIQUID AND VAPOR DISPOSAL

Revisions to the Phase I Interim Report

March 7, 1974

by R.W. Newman and James Little

MECHANICAL ENGINEERING DEPARTMENT
FLORIDA INSTITUTE OF TECHNOLOGY
Melbourne, Florida 32901

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

John F. Kennedy Space Center

Contract NAS 10-8399

Approved by:

T. E. Bowman

Thomas E. Bowman
Study Manager

FOREWORD

This document consists of revisions to the Phase I Interim Report, by T. E. Bowman and R. W. Newman, dated 28 December 1973. The revisions consist of three items:

1. Table I, "Contacts and Responses by Category", appearing in Section II. B, page 4 of the Interim Report, has been expanded to include additional information, as per the request of the Contracting Agency.

2. Section II, Appendix A, page 14 of the Interim Report has been corrected. McDonnell Douglas Astronautics Company was inadvertently omitted from the original list, Thermal Research and Engineering Corporation was listed with an incorrect address, and Instel Corporation should not have been included.

3. Section IV has been added to Appendix A. This section consists of a complete list of all organizations contacted, according to type of response or absence thereof, in accordance with the contracting Agency's request. This section should be added between pages 20 and 21 of the Interim Report.

In addition to these revisions, an Addendum to the Interim Report entitled "Chemistry of Hypergolic Propellant Disposal Systems" has been prepared as a separate document, dated March 4, 1974, by Henry Sivik.

TABLE I

CONTACTS AND RESPONSES BY CATEGORY

Category	Response				
	Positive		Negative	Zero	
	Techniques	Suggestions		No Response	Letter Return
Chemical & Manufacturers	8	1	9	14	5
Users	9	4	3	6	0
Equipment Manufacturers	4	0	9	3	0
Other	10	1	1	1	1
Totals	31	6	22	24	6

A - II. LIST OF COOPERATING ORGANIZATIONS

Aerojet Liquid Rocket Co., Sacramento, California
Allied Chemical Corp., New York, New York
Battelle Columbus Laboratories, Columbus, Ohio
Battelle Pacific Northwest Laboratory, Richland, Washington
Bell Aerospace Co., Buffalo, New York
The Boeing Company, Seattle, Washington
E.I. Du Pont de Nemours and Co., Inc., Wilmington, Delaware
Fairmount Chemical Co., Newark, New Jersey
Fisons Ltd., Cambridge, England
FMC Corp., New York, New York
Hercules, Inc., Wilmington, Delaware
Lockheed Missiles and Space Co., Sunnyvale, California
Marquardt Co., Van Nuys, California
Martin-Marietta Corp., Denver, Colorado, and Vandenberg AFB, Calif.
McDonnell Douglas Astronautics Co., Huntington Beach, California
NASA - Johnson Space Center, Houston, Texas
NASA - Western Test Range
NASA - White Sands, New Mexico
Olin Chemicals, Stamford, Connecticut
Pan American World Airways, Cape Canaveral, Florida
PPG Industries Inc., Pittsburgh, Pennsylvania
Rockwell International, Rocketdyne Div., Canoga Park, California
Rockwell International, Space Div., Downey, California
SAAB - Scania Ab, Linkoping, Sweden
Shell Development Co., Houston, Texas
Sundstrand Aviation, Rockford, Illinois
Thermal Research and Engineering Corp., Conshohocken, Pennsylvania
Tri-Mer Corp., Owosso, Michigan
TRW Systems, Redondo Beach, California
United Aircraft, Hamilton Standard Div., Windsor Locks, Connecticut
United Aircraft, United Technology Center, Sunnyvale, California
Volvo Flygmotor Ab, Trollhattan, Sweden
Walter Kidde and Co., Inc., Belleville, New Jersey

We would also like to thank the many other companies who wrote or telephoned to let us know that they had no significant information to contribute.

A - IV. COMPLETE LIST OF ORGANIZATIONS CONTACTED

A. Positive Replies - Techniques

Aerojet Liquid Rocket Co., Sacramento, California
Allied Chemical Corp., Solvay, New York
Battelle Columbus Laboratories, Columbus, Ohio
Bell Aerospace Co., Buffalo, New York
E.I. DuPont de Nemours & Co., Wilmington, Delaware
Fisons Limited, Cambridge, England
FMC Corp., Environmental Equipment Div., Chicago, Illinois
FMC Corp., Industrial Chemical Div., New York, New York
Hercules Inc., Wilmington, Delaware
Marquardt Co., Van Nuys, California
Martin-Marietta Aerospace, Denver Div., Denver, Colorado
Martin-Marietta Aerospace, Vandenburg AFB, California
McDonnell Douglas Astronautics Co., Huntington Beach, California
NASA - Johnson Space Center
NASA - Western Test Range
NASA - White Sands, New Mexico
Olin Chemicals, Stamford, Connecticut
Pan American World Airways, Cape Canaveral, Florida
PPG Industries, Inc., Pittsburgh, Pennsylvania
Rockwell International, Space Div., Downey, California
Shell Development Co., Houston, Texas
Sundstrand Aviation, Rockford, Illinois
Thermal Research & Engineering Corp., Conshohocken, Pennsylvania
Tri-Mer Corp., Owosso, Michigan
TRW Systems, Redondo Beach, California
United Aircraft, Hamilton Standard Div., Windsor Locks, Connecticut
United Aircraft, United Technology Center, Sunnyvale, California
USAF Eastern Test Range, Cape Canaveral, Florida
USAF Western Test Range
Volvo Flygmotor Ab, Trollhattan, Sweden
Walter Kidde & Co., Inc., Belleville, New Jersey

Positive Replies - Suggestions

Battelle Pacific Northwest Laboratory, Richland, Washington
Boeing Aerospace Co., Seattle, Washington
Fairmount Chemical Co., Inc., Newark, New Jersey
Lockheed Missiles & Space Company Inc., Sunnyvale, California
Rockwell International, Rocketdyne Div., Canoga Park, California
SAAB - Scania, Linkoping, Sweden

B. Negative Replies

A and S Corp., Verona, New Jersey
Alloychem Inc., New York, New York
American Chemical & Refining Co., Inc., Waterbury, Connecticut
Chemec Processes Systems, Inc., Tappan, New York
Dow Chemical Co., Midland, Michigan
Envirogenics Systems Co., El Monte, California
European Aerospace Corp., Greenwich, Connecticut
FECO, Cleveland, Ohio
Hawker Siddeley Dynamics LTD., Herts., England
ICN - K & K Laboratories, Plainview, New York
Industrial Chemical and Dye Corp., New York, New York
Instel Corp., New York, New York
Joy Manufacturing Co., Denver Equip. Div., Denver, Colorado
Kuehne Chemical Co., Elizabeth, New Jersey
Mallinckrodt Chemical Works, St. Louis, Missouri
McKesson Chemical Co., New York, New York
National Distillers and Chemical Corp., U.S. Industrial Chemical Co., Div., New York, New York
National Polychemicals, Inc., Wilmington, Massachusetts
Seymour MFG. Co., Seymour, Indiana
Space General Co., El Monte, California
Universal Oil Products Co., Des Plaines, Illinois
Westinghouse Electric Corp., Infilco Div., Richmond, Virginia

C. No Reply

City Chemical Corp., New York, New York
Combustion Engineering Inc., Chicago, Illinois
Engelhard Minerals and Chemical Corp., Engelhard Industries Div., Orlando, Florida
Environment One Corp., Schenectady, New York
Erno Raunfahrttechnik GMBH, Bremen, West Germany
Farbenfabriken Bayer A. G., Leverkusen, West Germany
Hikari Chemical Industries Co., LTD., Ohmiya City, Japan
Japan Hydrazine Co., Tokyo, Japan
Jones Chemicals,Inc., Caldonia, New York
Kraft Chemical Co., Chicago, Illinois
Messerschmitt - Boelkow - Blokm GMBH, Munich, West Germany
Mitsubishi Heavy Industries, LTD., Tokyo, Japan
Monopole des Pourdes, Toulouse, France
Mutchler Chemical Co., Inc., New York, New York
Office National Doetudes et de Recherches Aerospatiales, Chatillon, France
Otsuka Chemical Co., Osaka, Japan
Pennsalt Chemicals Corp., Philadelphia, Pennsylvania

Rocket Research Corp., Redmond, Washington
Shepard Chemical Industries,Inc., New York, New York
Societé des Produits Doazotes, Lannemezan, France
Societé Européene de Propulsion, Puteaux, France
Technologieforschung GMBH, Stuttgart, West Germany
TRW, Inc., Environmental Services, Redondo Beach, California
Uniroyal, Inc., Naugatuck, Connecticut

D. Not Deliverable

Astroage Corp., Buffalo, New York
E.R. Squibb and Sons, New York, New York
Ogden Technology Labs, Inc., Farmingdale, New York
Quimica Sintetica, Madrid, Spain
Seaway Chemical Corp., Buffalo, New York
Whiteley Hydraulics, Inc., Melrose, Massachusetts